Developing analytical methods for some additives and studying their behavior in mineral insulating oils

BY

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Dissertation Abstract

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TITLE OF STUDY : Developing analytical methods for some additives and studying their behavior in mineral insulating oils

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2,6-Di-tert-butyl-p-cresol, (DBPC), dibenzyl disulfide, (DBDS), and 1,2,3-benzotriazole, (BTA), are additives may be found concomitantly in the matrix of the power transformer oil. DBPC and DBDS act as antioxidants while, BTA is a corrosion inhibitor that protects copper conductors inside the transformer from the effect of even traces of organic sulfur compounds such as DBDS. This work describes a unique single liquid-liquid extraction pretreatment step using n-hexane as diluent for the oil sample and acetonitrile as an extractant thus, the three components are extracted simultaneously before injection into either GC or HPLC system. DBDS and DBPC are simultaneously determined using GC technique with a dual detector (ECD and FID). Another portion of the extract is injected into an HPLC-UV to determine BTA. This quantitative procedure has the advantage of low chemical consumption as well as being less laborious and less time consuming. The results indicate that the method is sensitive,

accurate, precise and linear with $R^2 > 0.99$ for each component. The resulting detection limits 0.01% (w/v), 0.80mgL^{-1}, and 2.04 mgL^{-1} for DBPC, DBDS and BTA respectively were lower than those obtained by the standard methods. The method can be used for both fresh and used mineral insulating oil. Using this analytical procedure, the behavior of DBDS as corrosive sulfur species has been investigated in mineral insulating oils. The critical DBDS concentration and temperature for copper sulfide formation were estimated kinetically to be less than 9 mgL^{-1} DBDS and 100° C respectively. The minimum effective BTA concentration was also determined to be 5 mgL^{-1} that retards copper sulfide formation. Also the study confirmed that DBDS remains in mineral insulating oil for long time before being subjected to chemical depletion when it acts as either as antioxidant or as corrosive sulfur. The synergy effect between corrosive sulfur (DBDS), primary antioxidant (DBPC) and metal passivator (BTA) in mineral insulating oil was also qualitatively and quantitatively investigated in the current work.

ملخص الدراسة

الاسم	**نـمر أحمد مهنا**
عنوان الرسالة	**تطوير طرق تحليل لبعض الإضافات الكيميائية ودراسة سلوكها في زيوت العزل للمحولات الكهربائية**
التخصص	**كيمياء تحليلية**
التاريخ	**أكتوبر 2011**

ثنائي بنزيل ثنائي الكبريتيد DBDS و ثنائي بوتيل بارا كريزول DBPC و البنزوتريازول BTA تعتبر مضافات في زيوت المحولات حيث قد تتواجد معاً أو كلاً على حدة في زيوت العزل للمحولات الكهربائية ذات المنشأ البترولي . DBPC و DBDS يعتبران كموانع أكسدة في هذه الزيوت بينما يتصرف BTA كمانع تآكل والتي تحمي لفائف النحاس داخل المحول من التلف من آثار الكبريت العضوي إن وجد في الزيت مثل DBDS والتي تؤدي في النهاية إلى مشاكل كهربائية وأعطال غير متوقعة في المحول . تصف الدراسة الحالية طريقة تحليل مميزة باستخدم خطوة إستخلاص سائل – سائل واحدة فقط بواسطة مذيب الأسيتونيتريل القطبي والهيكسان غير القطبي ، وعليه يتم إستخلاص المضافات هذه من الزيت قبل حقنها في جهازي الكروماتوغراف الغاز والسائل . يتم تحليل بهذه الطريقة كلاً من DBDS و DBPC بشكل آني باستخدام الكروماتوغراف الغازي . أما BTA يتم تحليله على الكروماتوغراف السائل . تتميز طريقة التحليل باستخدام أقل قدر ممكن من المحاليل وتتطلب وقت أقل في التحضير . تبين النتائج أن الطريقة الجديدة ذات حساسية ودقة عاليتين سواء لتحليل زيوت المحولات الجديدة والمستخدمة . أقل كمية تم تحديدها بواسطة هذه الطريقة لكل من DBPC و DBDS و BTA كانت 0.01% w/v ، 0.80 mgL^{-1} ، 2.04 mgL^{-1} على التوالي . باستخدام هذا الإجراء التحليلي تم دراسة سلوك مركب DBDS

في زيوت المحولات ذات المنشأ البترولي . تم دراسة أقل تركيز لمادة DBDS إضافة للحرارة الحرجة التي لو توفرت تلك الظروف يبدأ العمل كمادة تآكل وذلك على النحو التالي $9\ mgL^{-1}$ و 100 درجة مئوية على التوالي . أيضاً تم تحديد التركيز الحرج لمادة BTA حيث أقل من هذا التركيز ($5\ mgL^{-1}$) يبدأ مفعول التآكل بواسطة DBDS إن وجد في الزيت . إضافة لذلك فقد استنتج أن مادة DBDS ثابتة كيميائياً وقد تبقى فترة طويلة في الزيت قبل أن تتفكك . سلوكاً آخر تم تحديده بواسطة الإجراء التحليلي السابق حيث أن المفعول المعاون لمادة BTA من قبل مادة DBPC على مشكلة التآكل داخل المحولات الكهربائية ليست مهمة وبالتالي ليس لها آثر على إيقاف التآكل على صفائح النحاس داخل المحول .

Chapter One

Chemistry of mineral insulating oil and analytical testing for some of its additives

1.1 Introduction

The first transformer which was built by George Westinghouse 100 years ago used oil, copper, cardboard and steel. These raw materials are still in use for today transformers. Furthermore, while there have been many changes in crudes, processing, additives and extractions, the basic insulating oil still exhibits a reliable performance [1].

Insulating oil should have important properties that are considered mandatory to be monitored during the oil operational life. As per the ASTM Standard, D 2864-07 (Standard Terminology Relating to Electrical Insulating Liquids and Gases) insulating oil can be described as "dielectric" that is defined as a medium in which it is possible to maintain an electric field with little supply of energy from outside sources. Alternatively it may be described as "insulating material" that is defined as a material of relatively low electrical conductivity and high dielectric strength. This oil is usually used to support and provide electrical separation for conductors. Insulating oil acts as an insulating liquid or gas which does not readily conduct electricity. Electrical insulating fluids typically provide both electrical insulation and heat transfer in electrical equipment.

Myers and his co-authors stated in their book, Transformer Maintenance Guide [2], that some people refer to anything other than air inside a transformer is considered as “oil”. So, the term “transformer oil” may really mean “insulating fluid”. Hence, the term insulating oil or mineral insulating oil will be adopted in this study. In general, mineral insulating oil can be defined as an oil of mineral origin, refined from petroleum crude and has electrical insulating properties. Specific chemical and physical properties should be monitored to maintain the insulating properties of such type of oil. Certain parts of the electrical transformer unit like the copper windings are generally covered with Kraft insulating paper and immersed in the mineral insulating oil.

1.2 Insulating oil chemistry

Normally, four functions are expected to be fulfilled by the mineral insulating oil. Thus, these functions must be routinely monitored by applying a maintenance program for all electrical transformers. These functions are summarized as follows:

- Oil provides dielectric strength (dielectric and insulating material).
- Oil provides heat transfer (cooling medium).
- Oil protects the solid insulation (barrier between the paper and the damaging effects of oxygen and moisture).
- Oil can be tested to give an indication of conditions inside the equipment (diagnostic tool).

The chemical composition of insulating oil is very complicated, and it is usually composed of both hydrocarbon and non-hydrocarbon compounds. Hydrocarbon compounds form the major constituent of insulating oil matrix which can be divided into paraffins, naphthenes

and aromatic hydrocarbons. The non-hydrocarbons (hetero compounds) of insulating oils include naphthenic acids, esters, alcohols, nitrogen and sulfur compounds [3].

Some hetero compounds are essential for insulating oil performance and quality whereas some compounds are undesirable for such matrix. Compounds which contain amino acids and phenol groups together act as antioxidants in the insulating oil and are thus desirable compounds. The same is considered for some thermally stable sulfur compounds where they act also as antioxidants in the oil matrix. The availability of acidic compounds must be always prevented in such sensitive matrix of mineral oils.

When the insulating oil is subjected to deterioration (degradation) due to loading or aging effect, the chemistry system will be changed and the oil becomes reactive. Testing the new and/or in-service insulating oils gives a clear conclusion about the quality status of the whole unit. Furthermore, chemical testing of the insulating oil is considered a powerful diagnostic tool which can predict and detect faults. Chemical bonds in the hydrocarbons of insulating oils may break at certain circumstances and form radical species in the oil matrix. These radicals may recombine in random criteria to produce undesirable by-products called oxidation or aging by-products. These undesirable by-products are either acids, aldehydes, esters, ketones, peroxides, or alcohols. These by-products not only affect the insulating properties of the oil, but also form a sludge which modifies the heat transfer properties of the oil and eventually will destroy the major function of the oil [4]. These by-products are detected and evaluated using analytical standard methods by testing the oil matrix. There are several standard organizations that test and evaluate the quality of the insulating oil.

American Standard for Testing Materials, ASTM, develops standard methods for testing insulating oil including standard specifications of the oil. International Electrotechnical Commission, IEC, is an European standard devoted for the same purpose. Institute of Electrical and Electronic Engineers, IEEE, is considered as interpretation tool for ASTM standards.

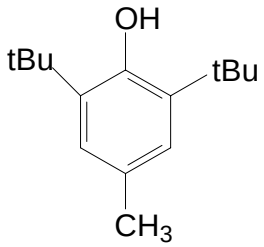
Factors that accelerate of oil deterioration are well understood nowadays [5]. Oxidation is mainly caused by exposure to high operational temperatures in presence of oxygen, metals and moisture in oil matrix. Oxygen from air inside the transformer exists as dissolved oxygen and has a relatively higher solubility compared with nitrogen. It is well known that high oxygen content catalyzes the deterioration as well as the oxidation processes of the oil. Another factor is the moisture content in oil where water can enter into the insulating oil externally via a leak or internally as a by-product of an oxidation process. Water is considered as a major catalyst for oil oxidation, while heat is a major accelerator for the chemical reactions. The operating temperature of the transformer affects the rate of the oxidation process. For instance, at a temperature of 100° C a period of five days is enough for oxidation to take place. However several months are required to complete the oxidation process at 75° C.

1.3 Significance of Insulating Oil Properties and Testing

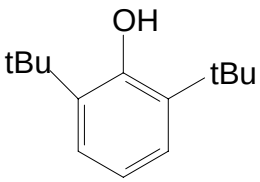
Being a refined mineral oil obtained from the fractional distillation of crude oil, insulating oil should be free from moisture, inorganic acids, alkali, sulfur, asphalt, tar and other types of oil matrices. Normally, insulating oil has the following properties [1]:

1. High dielectric strength.
2. Low viscosity.
3. Freedom from inorganic acids, alkali, corrosive sulfur.
4. Good resistance to emulsification.
5. Freedom from sludge under normal operation.
6. Low pour point.
7. High flash point.

To prevent the oxidation processes inside the oil matrix, the transformer manufacturers make significant efforts to insure that the unit tank or case is well sealed from atmosphere. Vacuum processing is conducted to remove air and moisture prior to sealing. The tank is filled with nitrogen to minimize penetration of oxygen. It is known that oil matrix with dissolved oxygen of more than 2000 mg L^{-1} initiate the oxidation processes. Oxidation activities in the oil can be further reduced by antioxidant additives or oxidation inhibitors. Antioxidants are occasionally added with other additives to insulating oil. There are several compounds that have been proposed as oxidation inhibitors or antioxidants in which the formation of radicals and by-products are retarded and controlled in the oil matrix. 2,6-di-*tert*-butyl-*p*-cresol (DBPC) and or 2,6-di-*tert*-butyl-phenol (DBP) are the most famous and useful antioxidants that are used in this regard as radicals trapping agents.



2,6-di-*tert*-butyl-*p*-cresol (DBPC)



2,6-di-*tert*-butyl-phenol (DBP)

DBPC is widely used in insulating oil applications to catch the radicals generated by the oxidation process of hydrocarbons and consequently prevents degradation of insulating oil [6]. The commercially available insulating oils are produced from base oils, mainly of mineral origin. ASTM D-3487 [7] classifies new mineral insulating oils into two types, regardless the origin of the crude oil and the refining process. Oils of type I are moderately resistant to oxidation whereas those of type II present a high resistance to oxidation. The oils of type I are commercialized without antioxidant addition, since they contain natural inhibitors. On the contrary, artificial inhibitors must be added to oils of type II in order to enhance their stability [4].

Oxidation inhibitors when added to oil should be in the range of 0.2% to 0.3% inhibitor. Uninhibited oil should be in the range of minimum “none detected” to maximum 0.08%. In DBPC the hydroxyl–OH group is sterically hindered by *tert.butyl* group. The result is something like a protective shield and the –OH group cannot take a coplanar position with the aromatic nucleus. As a result of the effect of the *tert.butyl* groups the aromatic nucleus is not completely planar and the –OH group is nearly perpendicular to the aromatic nucleus. This screening of the –OH group makes it hardly accessible for Van der Waals interactions [5].

Removing moisture content from the oil matrix is also an easy process during transformer unit installation. Moisture can be removed by oil circulation under vacuum.

Transformer unit design can be modified some time to reduce and control the operating temperature of the electrical transformer. This is considered essential to prevent the decomposition of the oil structure which is usually initiated by heat. Overloading the transformer during operation is the major reason of heating problems.

The chemical testing for the quality of the oil is not expensive compared to the damage that can occur due to the deterioration of the oil. Therefore, testing should be done as part of a well designed and implemented maintenance program. When test data are incorporated into a proper maintenance program, operation is improved and this results in a more cost effective approach to meet the maintenance needs.

The analytical requirements needed to evaluate new insulating oil's quality are listed in the ASTM D3487 that refers to two types of insulating oil, un-inhibited (type I) and inhibited (type II) in which the level of antioxidant additives is varied only. All of the listed properties are important to manufacturers where some properties have higher levels of importance than others. In addition, the properties have more significance in different areas of considerations. Some properties are used for design calculations, others are used to indicate the uniformity of the oil from the producers, and some are used to reveal normal or abnormal operation of the apparatus in service.

1.4 Corrosive sulfur problems in insulating oil

Corrosive sulfur detection in insulating oil is considered as a routine analytical parameter. However, long time ago this was not a critical or a serious concern for insulating oil

functionalities. Several transformer units have failed during the last five years [8] although their results of the quality control tests were satisfactory. A worldwide confusion has resulted about the reasons behind such unexpected and uncontrolled failures. Several reports were published about the reasons of unexpected failures in transformer units. The majority of these reports concluded that the formation of copper sulfide (Cu_2S) due to organic sulfur compounds in transformer insulation is the main reason behind those failures. Even though it has only recently been recognized as a serious problem, the re-examination of old failure cases indicated that the problem is not new. However, there is little doubt that the problem has been increasing in recent years [9].

Organic sulfur compounds usually exist in the crude oil matrix. Crude oil consists of different types of hydrocarbons that can be classified as paraffinic, naphthenic and aromatic hydrocarbons mixed together [3]. It was found that naphthenic hydrocarbons, naturally, contain less organic sulfur compounds. So, due to the requirements for low sulfur mineral oil, there has been a marked decrease in the concentration of total sulfur compounds in mineral insulating oils during the past 15 years, where the sulfur concentration was dropped from about 6000 kg kg^{-1} in 1964 into few mg kg^{-1} [10]. This reduction in total sulfur concentration was accomplished through improvements in the petroleum refining processes including the introduction of the hydro-treating in 1989 – 1990, as a technique mainly for the production of naphthenic bases. The reduction in total sulfur is accompanied by reduction in concentrations of aromatics and heteroatom organics in mineral insulating oils. The reduction in organosulfur compounds may lead to reduction in the natural antioxidant contents of the mineral oils [10]. Some of these organic sulfur compounds are chemically

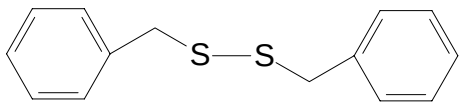
stable and can be used as antioxidants in the oil matrix to avoid the undesirable oxidation processes when the oil starts deteriorating. Organic sulfur compounds where the sulfur atom is involved in an aromatic structure (e.g thiophenes) are usually considered as non reactive and not harmful to metallic parts inside a transformer [11 - 12]. On the other hand, other existing sulfur compounds like mercaptens, benzyl sulfides and free sulfur have sever effects against the conductor plats (copper and iron) inside the transformer unit and these sulfur compounds are considered as corrosive to the metallic parts inside the transformer.

The primary effect of the sulfur species in insulating oil is the formation of copper sulfide (Cu_2S) on the surface of copper conductors and its subsequent migration through the insulating paper layers, leading to electrical faults [13]. This corrosion causes a progressive degradation of the insulating property of both the oil and the cellulose material inside the transformer unit by injecting conductive particles like copper sulfide into the oil matrix. Recent investigations were conducted on copper sulfide formation inside electrical transformer units. Such investigations helped the identification of the class of organic sulfur compounds responsible for the formation of copper sulfide [10]. It was concluded that disulfides were found at high concentrations whereas other organic sulfur forms were detected at trace levels.

1.4.1 Dibenzyl disulfide (DBDS) as a main corrosive sulfur species in insulating oil

The mechanism of copper sulfide formation in transformers and reactors has been intensively studied worldwide in recent years. Various methods have been proposed to

investigate the source of copper sulfide formation. It has been revealed that most malignant oils contain dibenzyl disulfide (DBDS) [14].The majority of these investigations indicated that DBDS is the main reason for the formation of copper sulfide inside the electrical units. Consequently all the unexpected operational failures have been attributed to the presence of DBDS. CIGER WG A2-32 report [9] have stated clearly that “oils containing reactive sulfur species, identified in most cases as dibenzyl disulfide (DBDS), can react with copper to form copper sulfide on the surface of the conductors and on the paper insulation surfaces, even under the normal operating conditions of the transformer. However, it is far from obvious how copper can be transported into the layers of covering paper, or onto cellulose surfaces facing the oil”. Another study was conducted by Amimoto et al [15] and has supported the statement of CIGER WG A2-32 report. It was concluded that “ reducing DBDS concentration in oil is very effective in suppressing the copper-sulfide deposition. Reducing DBDS concentration by half is considered to double the lifetime of transformers and reactors”. Other investigations have shown that dibenzyl disulfide is one of the main substances causing the deposition of copper sulfide on insulating paper in which the deposition rate is proportional to the DBDS concentration [16 - 18].



dibenzyl disulfide (DBDS)

According to the above mentioned results, oil producers are trying to minimize the total sulfur in insulating oil. However, dibenzyl disulfide, DBDS, was used by some other oil

manufacturers as an antioxidant additive to retard the oxidation processes. They thought that the sulfur added as DBDS would have a minor effect because of its low concentration compared to that originally introduced from a natural origin [11]. Most studies about the availability of DBDS in insulating oil confirmed that such compound cannot exist as natural organic sulfur compound in the oil matrix since DBDS decomposes at 270° C and its reactivity beyond this temperature would disappear [12].

During the refining processes the temperatures may rise up to more than 270° C, consequently DBDS, if present in the oil naturally, it should decompose at this elevated temperature. Thus, when DBDS is detected in insulating oil, it must be coming from an external source where it has been added as an antioxidant. Using DBDS as an antioxidant and as a stabilizer for petroleum distillates and polymers have been reported [19]. A relatively large percentage of commercially available mineral insulating oils have been found to contain DBDS where it exists as an undeclared artificial antioxidant additive [10].

Several factors have been proposed [9, 12, 14, 17, 18] to study the real behavior of DBDS which leads to copper sulfide deposition inside transformer unit parts. Temperature is considered as the main factor in forming copper sulfide. Oxygen is another important factor that supports the presence of copper sulfide in insulating oil. High electrical stress activity inside the transformer unit also initiates copper sulfide formation when DBDS is available in the oil matrix. Localized overheating (hot-spots) and arcing in the transformer unit increase the rate of copper sulfide deposition on the insulating paper and copper conductors.

Other factors like the type of the insulating paper used has no significant effect on the formation of Cu_2S.

The mechanism of copper sulfide Cu_2S deposition was suggested by Toyama et al [20] and can be divided into two stages. The incubation stage and the deposition stage which are given below.

Step 1 Formation of DBDS-Cu complex

$$2Cu + (C_6H_5CH_2)_2S_2 \longrightarrow (C_6H_5CH_2)_2S_2\text{-}Cu_2 \quad \text{.....(1)}$$

Step 2 Formation of copper sulfide and by -products

Step 2.1 Formation of copper sulfide

$$(C_6H_5CH_2)_2S_2\text{-}Cu_2 \longrightarrow Cu_2S + C_6H_5CH_2^{\bullet} + C_6H_5CH_2S^{\bullet} \quad (\bullet \text{ radical})$$

Step 2.2 Formation of by-products

$$4\,C_6H_5CH_2^{\bullet} + 4C_6H_5CH_2S^{\bullet} \longrightarrow$$
$$C_6H_5CH_2CH_2C_6H_5 + 2(C_6H_5CH_2)_2S + (C_6H_5CH_2)_2S_2 \quad \text{.....(2)}$$

Equations (1) and (2) can be combined to give equation (3)

$$8Cu + 3(C_6H_5CH_2)_2S_2 \longrightarrow$$
$$4\,Cu_2S + C_6H_5CH_2CH_2C_6H_5 + 2(C_6H_5CH_2)_2S \quad \text{.....(3)}$$

Furthermore, DBS formed in equation (3) react with copper

$$2Cu + (C_6H_5CH_2)_2S \longrightarrow Cu_2S + C_6H_5CH_2CH_2C_6H_5 \quad \text{.....(4)}$$

Then equation (3) and (4) can be combined to give equation (5)

$$4Cu + (C_6H_5CH_2)_2S_2 \longrightarrow 2Cu_2S + C_6H_5CH_2CH_2C_6H_5 \quad \text{.....(5)}$$

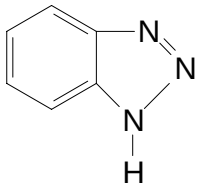
According to Toyama et al [20], copper sulfide formation on insulating paper should occur via DBDS-Cu complex at low temperature. Copper sulfide and the radical intermediates are generated by the decomposition of Cu-DBDS complex.

In general, the transformer unit is unlikely to fail as soon as there is some precipitation of copper sulfide. On the contrary, some transformer windings contain a lot of copper sulfide and still do not fail. At the end, the failure is caused by a combined effect of the weakening of the insulation and the dielectric stresses that the winding experiences.

1.4.2 Mitigation procedures for corrosive sulfur problem in insulating oil

The most common mitigation procedure to resolve corrosive sulfur formation in insulating oils is the addition of metal passivators. Passivation is a term used in corrosion science to describe the formation of non-permeable surface layers on metals. Therefore, oil passivation is a process that is carried out after having a positive result for corrosive sulfur in an insulating oil sample. The passivator is an organic nitrogen compound that is added to the oil matrix to protect copper conductors inside the electrical transformer from further corrosion with active organic sulfur. These additives compete with DBDS for the reaction with copper, where they form a copper complex, thus the reaction with DBDS would be minimized and thus the corrosive sulfur formation would be inhibited. The reaction mechanism between copper conductors and metal passivators is well understood in which a compound such as benzatriazol (BTA) and its derivatives form an organometallic copper complex that is more stable than the complex between DBDS and copper [21 - 23]. This creates a thin molecular layer of BTA that prevents DBDS effect on copper. In aqueous solutions it is known that BTA forms thick multilayers on the copper surface. Such molecular layers were studied by mass spectrometric technique, TOF-SIMS, to confirm that at least monomolecular thickness was built up in matters of hours in the oil media. Also it was found that virtually no material left on the surface after re-emersion in passivator free

oil indicating irreversible binding [24]. According to step 1 in copper sulfide formation mechanism described before, the concentration of dissolved copper is significantly decreased when passivators are added to mineral insulating oil.



1,2,3-benzotriazole (BTA)

Examples of a widely used group of triazole-base passivators applied in mineral insulating oils are 1,2,3-benzotriazole (BTA), tolybenzotriazole (TTA) and aminomethylated derivatives Irgamet 39™ (CIBA Specialty Chemicals, Basel, Switzerland). Recent studies have shown that a synergetic effect might emerge when a passivator like (BTA) and an oxidation inhibitor (DBPC) both exist in the insulating oil at the same time [21]. BTA is a white powder whereas Irgamet 39^{TM} is a high viscous liquid at ambient temperature. Several tens to 100 mgL^{-1} of these substances are typically added to inhibit the reaction of copper with corrosive sulfur compounds. However, the addition of metal passivators is not a guarantee to prevent failures. For instance, in Brazil, more than 200 shunt reactor oils in service were passivated (in most cases between ½ and 2 years after going into service). It has been reported that nine of those units failed at a period of 1 – 24 months after passivation [11].

1.5 Analytical methods for detecting antioxidants, sulfur corrosive and passivator components of mineral insulating oil

The quality of the insulating oil depends on controlling the antioxidants, the corrosive and passivator species. These species are considered as quality control parameters and they have to be detected and controlled to avoid unexpected electrical problems during the operational process. Testing for these additives is also applicable for in-service oil especially those in electrical units without maintenance records. Monitoring of antioxidants and metal passivators levels in insulating oil matrix is also demanding where uncontrolled depletion may cause unexpected failures. Such monitoring requires sensitive analytical methods.

This study will focus mainly on three compounds, namely, dibenzyl disulfide, (DBDS), 2,6-Di-tert-butyl-p-cresol, (DBPC) and 1,2,3-benzotriazole, (BTA). Determining relatively low concentrations of these three components would help studying their interaction effects in the mineral oil and its corrosion and passivation actions under the transformer operational conditions. Traditionally, this interaction effect is studied indirectly by investigating the copper sulfide formation. Detecting and monitoring all available additives in the oil matrix is a recent demand in which corrosive sulfur, antioxidants and metal passivators need to be quantified at concentration levels as low as possible using accurate, precise and fast analytical techniques. A review covering the analytical techniques reported in the literature for the determination of each of the three species is given below.

1.5.1 Determination of corrosive sulfur (DBDS) in insulating oil

Few standard qualitative methods are available to detect the available organic sulfur compounds in insulating oil. American Society for Testing Materials, ASTM, and International Electrotechnical Commission, IEC methods are the most widely used for such determination [9, 25, 26]. However, some other limited quantitative methods are also reported in the literature.

The conventional standard method for the detection of corrosive sulfur compounds in insulating oils is ASTM D 1275 class A in which an insulating oil sample is incubated with a small copper strip at 140° C for 19 hours. At high temperature, corrosive sulfur in the oil matrix is more effective and approaches the copper strip under heat to form copper sulfide (the proposed mechanism for copper sulfide formation was previously mentioned) as an indication for corrosiveness in oil [27]. It was found that ASTM D 1275-A is not sufficient to detect more potential corrosive organic sulfur components in insulating oil, thus ASTM D 1275 class B method has been proposed as an alternative standard test to extend the incubation period of the sample into 48 hours in order to detect the most potential corrosive sulfur in the oil.

Also, an IEC 62535 method has been developed for the detection of corrosive organic sulfur in mineral oil. This method is based on simulation of conditions inside the transformer unit by incubating oil samples in two cramped glass headspace vials that are completely isolated from atmospheric air. One copper strip is immersed in the first vial while another similar strip is rapped with insulating paper and immersed in the second vial. The incubation is

made at 150° C for a period of 72 hours. The results obtained are interpreted according to the procedure adopted in the ASTM D 1275 test and the insulating paper is checked for the formation of copper sulfide.

D. Grant et al [28] designed a quantitative method based on a subtraction assay for the total reactive sulfur in insulating oils. Conditions similar to those of the ASTM D 1275-A and IEC-62535 were adopted in this work except that copper powder is used instead of a copper strip. This technique is a subtraction assay in which the total sulfur signal is recovered before and after the incubation process using fluorescence-based sulfur analyzer. Being qualitative only, the results obtained from the above methods would be incompetent in detecting DBDS in the presence of oil passivators. When a metal passivator is added to insulating oil, testing for the presence of DBDS and other organic sulfur contents by ASTM or IEC standards would reveal nothing about the corrosion of the metallic conductors in the transformer. Consequently, these results will give wrong conclusions to the end user which may lead to confusion about the availability of DBDS.

Unlike ASTM D 1275 and IEC 62535 methods, gas chromatography can separate and quantify DBDS in mineral oils at mgL^{-1} concentration levels and the detection of DBDS by GC methods is not affected by benzatriazol additives if present in insulating oil. The major challenge to detect DBDS in mineral oil using gas chromatography is to separate DBDS signal from the oil matrix which needs a pretreatment procedure. IEC proposed recently a new quantitative method for DBDS detection (IEC-62697-01) in both new and used insulating oil samples [29]. The method is based on diluting the oil sample to about 20 times

with isooctane followed by injecting the diluted sample into a gas chromatographic equipped with one of the following detectors: the electron capture detector (ECD), the mass spectrometer (MS) or the atomic emission detector (AED). Detection of organic sulfur in insulating oil is possible by GC-ECD as a result of sulfur electronegativity. DBDS contains two adjacent sulfur atoms with two pairs of lone electrons on each which allows detection by ECD. By using the dilution technique, oil matrix signal was reduced from the chromatogram signal assuming that ECD detector is not sensitive to hydrocarbons. It is expected that some available molecules in insulating oils may cause interferences in GC-MS methods. Dilution of the DBDS component in the oil to less than 5 mgL^{-1} would result in an insignificant signal for DBDS. According to this method, the presence of certain compounds especially polychlorinated biphenyls (PCBs) in mineral insulating oils can cause interference effect. In such cases a detector other than ECD should be used.

Toyama et al [20] introduced a quantitative method for the determination of DBDS in insulating oil using solid phase extraction, SEP, followed by GC-MS to recover and detect the DBDS signal. SPE was used to subtract the signal of the oil matrix from the signal of the chromatogram. This was performed by diluting the oil sample with hexane followed by passing the mixture through SPE using active alumina on which DBDS is adsorbed. DBDS was desorbed by benzene and then injected into the GC-MS system. The method is highly selective to DBDS and provides a quantitative conclusion. A detection limit of 0.1 mgL^{-1} DBDS was reported. Oil matrix signal was not fully removed from the chromatogram after using SPE treatment.

Another method was used for quantitative detection of corrosive sulfur in insulating oil by wavelength dispersive X-ray, WDX, technique which detects elemental sulfur as CuS deposited on a copper strip after artificial aging of the oil under heating. The technique showed a complicated analytical system for corrosive sulfur determination in insulating oil [30] and it was not selective for DBDS.

1.5.2 Determination of the oxidation inhibitor 2,6-di-*tert*-butyl-*p*-cresol (DBPC) in insulating oil

Monitoring DBPC level in the electrical insulating mineral oil is essential to confirm the performance of the antioxidant for reducing the formation of the oxidation by-products in insulating oils. Various methods are available to detect DBPC in mineral insulating oils. There are two ASTM standard methods developed for the quantitative detection of DBPC in insulating oil. ASTM D 4768 [31] is based upon using gas chromatography to determine DBPC in new and used insulating oils at concentrations up to 0.5% (w/w). This method is based on the separation of DBPC from oil sample by passing it through an alumina column followed by injection of the eluate into a gas chromatographic system equipped with FID detector. ASTM D 4768 has provided precise and accurate quantitative information about DBPC, however it is considered as a complicated, laborious and time-consuming technique [32]. Also due to variance between different batches of alumina, care must be taken to prepare both the working standards and test specimens by using the same batch of separation columns [31].

On the other hand, ASTM D 2668 was developed for the determination of DBPC by measuring its absorbance in the oil sample at 860 cm^{-1} using FTIR technique [33]. According to this method, the sample, without treatment, is introduced into an FTIR system and the absorbance is measured after the background correction is made using a calibration curve prepared for standard solutions measured in the same way. Although, FTIR technique is easy and fast, the background of the sample may not coincide with that of standard solutions, a matter that would reduce the accuracy and precision of the method. Furthermore, the technique is not sensitive, especially, when other oxidation byproducts absorb IR radiation at the same wavelength, thus the method may be not selective for DBPC and various deterioration by-products that developed as a function of aging time may interfere.

High performance liquid chromatography coupled with UV detector set at a wavelength of 283 nm has also been used for DBPC detection in new and aged insulating oil by Lamarre et al [32]. The mobile phase was a mixture of acetonitrile - water (97.5/2.5, v/v). The by-products resulted from oil oxidation in the aged oil and the oil components whose retention time in HPLC was identical to that of DBPC were eliminated by filtering the oil using silica cartridge. The method has a detection limit of 2.0 mgL^{-1}. Although silica cartridges were used in this method, chromatograms showed the oil background as a wide broad signal appearing just beside the analytical signal of DBPC, a problem that may not help for accurate quantification of DBPC specially in extremely deteriorated oil matrices.

DBPC in new and used transformer oil was also determined by differential pulse voltammetric technique using platinum microelectrode after eluting the sample with acetonitrile through a column of alumina under reduced pressure. The method achieved a detection limit of 10 mgL^{-1} [34].

Zamarreno et al [35] proposed a method for quantitative detection of DBPC using both solid phase extraction and liquid – liquid extraction as sample pretreatment before injection the eluat to micellar electrokinetic capillary chromatography. The silica SPE cartridge was conditioned first with 5 ml hexane then 2 ml oil sample containing known concentrations of DBPC (0.01 to 1.0%) was passed through the cartridge and the later was washed with 2 ml hexane. The retained DBPC was eluted with acetonitrile or methanol. A small portion of the extract was diluted with the separation buffer then injected into the electrokinetic capillary chromatography system. According to Zamarreño there was other inconvenience where the viscosity of the oil hinders its passage through the cartridge. In order to avoid this effect and to improve contact between the sample and solid phase, these procedures were modified, using oil samples diluted with hexane (1:3) and the elution with methanol or acetonitrile was carried out in the same way. As per Zamarreño, methanol and acetonitrile were used because these solvents have been used for the extraction of antioxidants in other matrices.

1.5.3 Determination of the metal passivator 1,2,3-Benzotriazole (BTA) in insulating oil

Using a passivator in insulating oil is a common protection procedure against corrosive sulfur. Monitoring the passivator content and the corrosion inhibitor, is a mandatory requirement nowadays. Augusta et al [36] investigated the need for monitoring passivator

content in insulating oil matrix. It was found that with uncontrolled depletion of passivator content, oil reverts to its original corrosion conditions leading to the deposition of copper sulfide on insulating paper and copper.

Analytical quantitative methods for BTA detection in insulating oil are limited. A recent new standard method has been released by the ASTM WK24216 for quantitative detection of Benzatriazol (BTA). The method covers the determination of the concentration of benzatriazol (BTA) and Irgamet 39™ in new and used electrical insulating oils by high performance liquid chromatography (HPLC) using UV detection. For new oils, this method aids in compliance monitoring of ASTM D 3487. For in-service oils, this method allows for the monitoring and quantitative determination of these additives. The method uses solid phase extraction (SPE) pretreatment where oil matrix is removed when injecting the sample into HPLC [37].

Another quantitative method has been proposed by the IEC-60666 [38] for detecting several passivators in insulating oil by HPLC using a similar technique of ASTM WK24216. This method is applicable for benzatriazol (BTA) detection. An oil sample is diluted with pentane and passed under vacuum through a silica gel SPE cartridge previously rinsed with methanol and pentane. The residue of nonpolar oil constituents retained by the solid phase is then eluted with a further volume of pentane and discarded. The cartridge is then dried by flushing it with air under vacuum. The analyte is eluted with a known volume of methanol and filtered through a 0,45 µm PTFE filter. The solution is then injected into HPLC system equipped with a reverse-phase column and BTA is detected with a UV detector at a

wavelength 260 – 270 nm. A similar method was previously established by Wiklund et al [23] using the same sample treatment and detection principle in which the oil sample was treated with SPE and injected in HPLC system for the detection of BTA to take place.

Solid phase extraction is not always a flexible analytical solution for sample pretreatment. Heavily oxidized oils may partially affect the analysis, giving relevant interferences from UV absorbing polar compounds. Sometimes standard addition method is used when SPE-HPLC technique is used to minimize the effects of the interferences resulting from polar compounds. The use of SPE as sample cleanup procedure adds more cost to the analytical process. Furthermore, and as per IEC-60666 method, SPE is a solvent consumption sample pretreatment technique in which nearly 50 ml solvent is needed to treat one oil sample for BTA detection before injecting to HPLC.

Chapter Two

Simultaneous liquid-liquid extraction of dibenzyl disulfide, 2,6-di-tert-butyl-p-cresol and 1,2,3-benzotriazole from power transformer oil prior to the GC and HPLC determination

2.1 Introduction

Chromatographic techniques are adopted in this work to avoid the limitations and difficulties encountered with the standard methods (as mentioned above) for corrosive sulfur detection in insulating oil. Gas chromatography is used for a simultaneous detection of DBDS and DBPC using dual detector ECD and FID respectively, whereas HPLC equipped with UV detector is used for BTA. Unlike the solid phase extraction sample treatment, the liquid-liquid extraction used in this study is performed with a minimal reagent consumption and less time.

This study was undertaken to investigate the efficiency of a single liquid-liquid extraction pretreatment step using a nonpolar diluent (n-hexane) for the oil sample and a polar solvent extractant (acetonitrile or methanol). Thus, DBDS, DBPC and BTA components are extracted from fresh and in service mineral insulating oil prior to their injection into either GC or HPLC systems. Simultaneous determination of DBDS and DBPC using GC technique with a dual detector is investigated. The passivator, BTA, after being extracted with the same solvent mixture was determined by HPLC-UV system. This new quantitative procedure should have the advantage of low chemical consumption, high sensitivity and low detection limits as well as being less laborious and less time consuming.

2.2 Experimental and methods

2.2.1 Chemicals

The chemicals used include: 2,6-di-*tert*-butyl-*p*-cresol (DBPC), internal standards diphenyl disulfide (DPDS) and diphenoxy benzene, dibenzyl disulfide (DBDS), 1,2,3-benzotriazol (BTA) (Aldrich); fresh mineral insulating oil meets the specifications of mineral insulating oils as per IEC-60296 [39] and free from DBPC, DBDS and BTA (a gift from the Gulf Chemical and Industrial Oils, Dammam, Saudi Arabia); acetonitrile, methanol and n-hexane (Merck). All chemicals used were of analytical reagent grade.

A stock solution of DBDS, DBPC and BTA was prepared by dissolving accurately weighed samples of these materials in fresh mineral insulating oil then diluting with oil as needed to give a solution having 1.0 % w/v DBPC and 100 mgL^{-1} DBDS and BTA. Various working standards of appropriate DBDS, DBPC and BTA concentrations were prepared from the stock solution according to the experimental needs. A stock solution of internal standard mixture of 0.2% diphenoxy benzene and 5 ppm DPDS was prepared in acetonitrile or methanol. The internal standards mixture was used for DBDS and DBPC detection through GC-ECD-FID. No internal standard was used for the determination of BTA using the HPLC method.

2.2.2 Instrumentation

Shimadzu GC, 17A Model, equipped with flame ionization detector, FID, electron captured detector, ECD, split/splitless auto injector and DB-5 column of 30m, 0.25mm, 1.00µm was used for DBDS and DBPC detection. The stationary phase for the column DB-5 is equivalent

to 5% phenyl polysiloxane and 95% methyl polysiloxane in which DBDS and DBPC are determined as per IEC-62697-01 and ASTM D 4768, respectively. Agilent HPLC, 1200 series, equipped with UV detector, auto-injector and ZORBAX Eclipse XDB-C18 column of 4.6 x 150 mm, 5 µm was used for BTA detection (equivalent to the one used in IEC-60666 for BTA detection). Tables 2.1 and 2.2 show the optimum GC and HPLC operating parameters for each compounds. 20 ml screw cap glass tubes were used for the liquid-liquid extraction. The cartridges used for solid phase extraction include: silica cartridge (500 mg SampliQ) and alumina cartridge (AccuBOND II Alumina N sorbents, with 50-200 µm particle size). A vacuum manifold for solid phase extraction from Millipore was used. 0.45 µm disposable filter syringes were used for HPLC solutions preparation.

2.2.3 Liquid-liquid extraction procedure

Fig 2.1 illustrates the liquid – liquid extraction procedure for the three species. 5 ml mineral insulating oil sample containing DBPC, DBDS and BTA was diluted with a certain volume of n-hexane (2 to 5 ml) in a 20 ml screw cap glass tube and 5 ml acetonitrile or methanol were added to function as an extractant for the three components simultaneously. The mixture was shaken vigorously for about 10 to 15 seconds then centrifuged at 2000 rpm for 1 minute.

For DBDS/DBPC determination, 2 ml of the acetonitrile or methanol layer was transferred into another tube and mixed with 2 ml of internal standard stock solution. This mixture was injected into GC-ECD-FID system. For BTA determination, 1 ml of the acetonitrile or methanol layer was transferred into another tube, 4 ml of deionized water was added to

Table 2.1 The optimum GC operating parameters for determination of DBDS and DBPC

Parameter	Setting
Initial temperature	150 ^{o} C for 1 min
Rate	17 ^{o} C/min
Final temperature	250 ^{o} C for 15 min
Injector temperature	250 ^{o} C
FID temperature	280 ^{o} C
ECD temperature	310 ^{o} C
Injector mode	Split/Splitless
Split ratio	10:1
Total flow	15.0ml/min
Linear velocity	32.2cm/sec
Column	DB-5 30m, 0.25mm, 1.00 μm
DBDS Signal (RT)	17.80 min
DBPC signal (RT)	7.70 min
Injection volume	1.5 μL

Table 2.2 The optimum HPLC operating parameters for determination of BTA

Parameter	Setting
Separation temperature	40 ^{o} C
Injector temperature	Ambient temperature
UV wavelength	250 to 260 nm
Injector mode	Auto
Pump mode	Binary
Flow rate	1.0 ml/min
Column	ZORBAX Eclipse XDB-C18 4.6 x 150 mm , 5 μm
BTA signal (RT)	3.60 min
Injection volume	10 μL

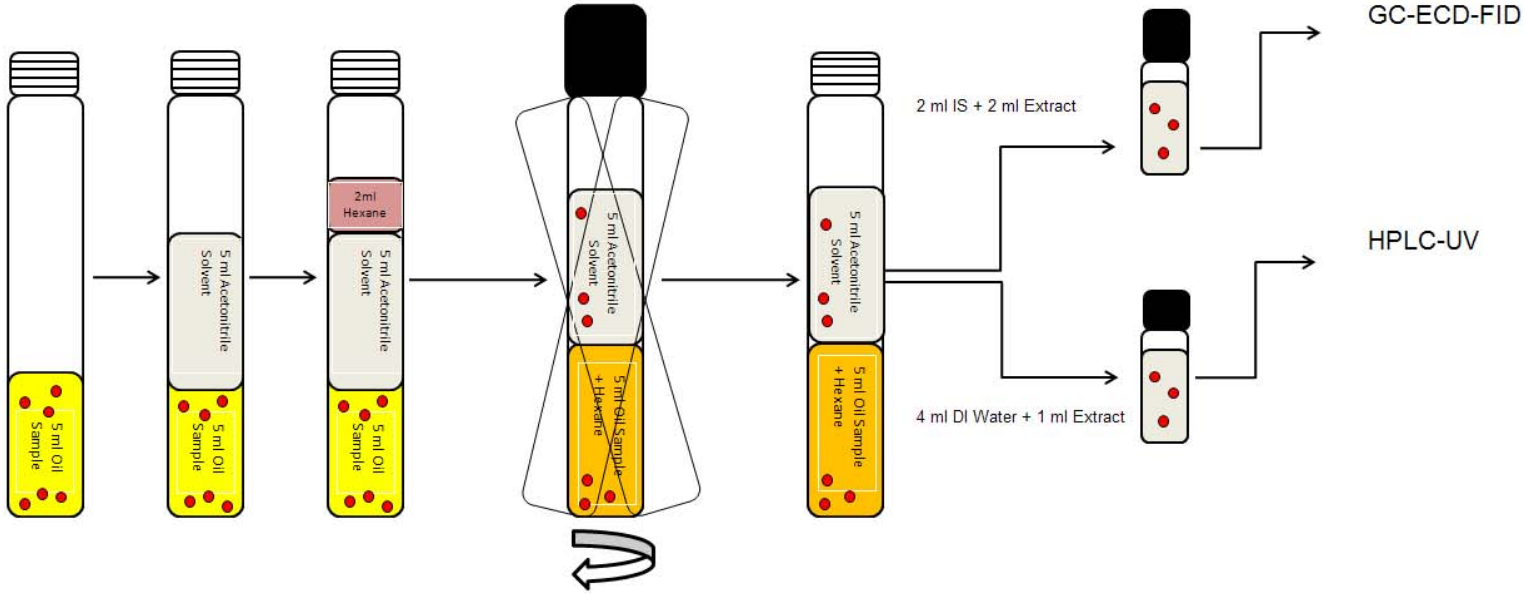


Fig 2.1. Flow diagram illustrating the sequence of extraction steps

match the mobile phase matrix (80:20 v/v water: acetonitrile). The mixture was filtered through 0.45 μm syringe filter and stored for HPLC-UV injection.

2.2.4 Solid phase extraction

Solid phase extraction experimental trials were tested in this work according to the literature/standard procedures [20, 31 and 38] with some modifications (instead of their home made clean up columns, readymade cartridges were used here) to examine the efficiency of solid phase extraction and the GC or HPLC signal sensitivity for each of the three components, individually, when injected into these systems after the solid phase extraction step. In all solid phase extraction trials, a mineral oil sample was diluted with n-hexane or n-heptane and eluted through an alumina or silica cartridge using a certain eluent. The sought component (DBDS or DBPC or BTA) was washed out from the cartridge using a desorbent agent that was benzene in the case of DBDS and methanol in the case of DBPC and BTA.

2.3 Results and discussion

2.3.1 Assessment of the liquid-liquid extraction pretreatment process

The individual determination of DBDS, DBPC and BTA in mineral insulating oil using GC or HPLC requires a pre-extraction step. This is due to the fact that the mineral oil matrix usually introduces a high background effect in the GC and HPLC chromatograms that obscures the signals of those compounds which are displayed in these chromatograms. Therefore, the determination of these components in the oil suffers from low sensitivity and poor precision especially when solid phase extraction step was applied prior to the

determination of DBDS, DBPC using GC method and BTA using HPLC method [20, 31, 38] where extensive dilution takes place during the elution process. In this work, a liquid-liquid pretreatment step is introduced and the results obtained are compared with those of the solid phase extraction step.

In the preliminary liquid-liquid extraction experimental trials, the extraction protocol was conducted using a liquid extractant (acetonitrile or methanol) to extract, simultaneously, the DBPC, BTA and DBDS contents of a mineral oil sample diluted with n-hexane. The layer comprising the three components was separated, diluted with internal standard if needed, then injected into the GC or HPLC system. The chromatograms were recorded and the peak area of each component was used for the assessment of the extraction efficiency of the component. For the sake of comparison, the known standard methods, ASTM D 4768, IEC-60666 and IEC-62697, were applied for the determination of DBPC, BTA and DBDS. According to these methods, GC and HPLC techniques were used for the determination of DBPC and BTA, respectively after solid phase extraction pretreatment step; while DBDS was determined without a pretreatment step but with significant dilution with isooctane to minimize the oil matrix background interference on the GC chromatogram.

The chromatograms obtained after liquid-liquid extraction showed that the background signal associated with the oil matrix was almost eliminated in the detection of DBPC using GC/FID system similar to what has been reported when solid phase extraction was used [20, 31, 38] (Figs. 2.2 and 2.3). However, the chromatographic peak areas of each of the three components were drastically enhanced (Figs. 2.3, 2.5 and 2.7) compared to those observed when determined by the standard methods mentioned above (Figs 2.4, 2.6 and 2.8).

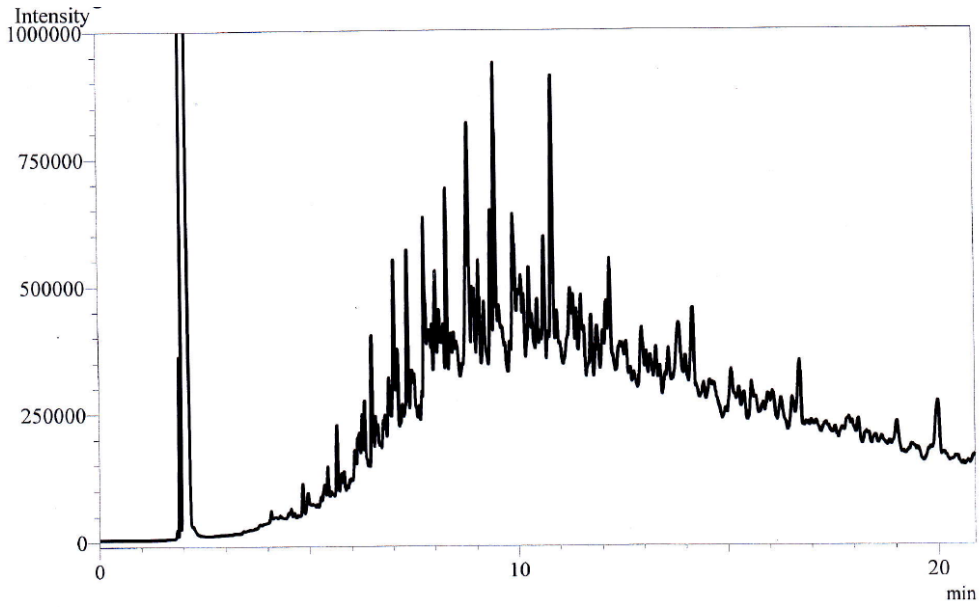


Fig 2.2. A chromatogram for insulating oil containing 0.2% DBPC in mineral oil diluted with n-hexane (oil:n-hexane; 5 : 2, v/v).

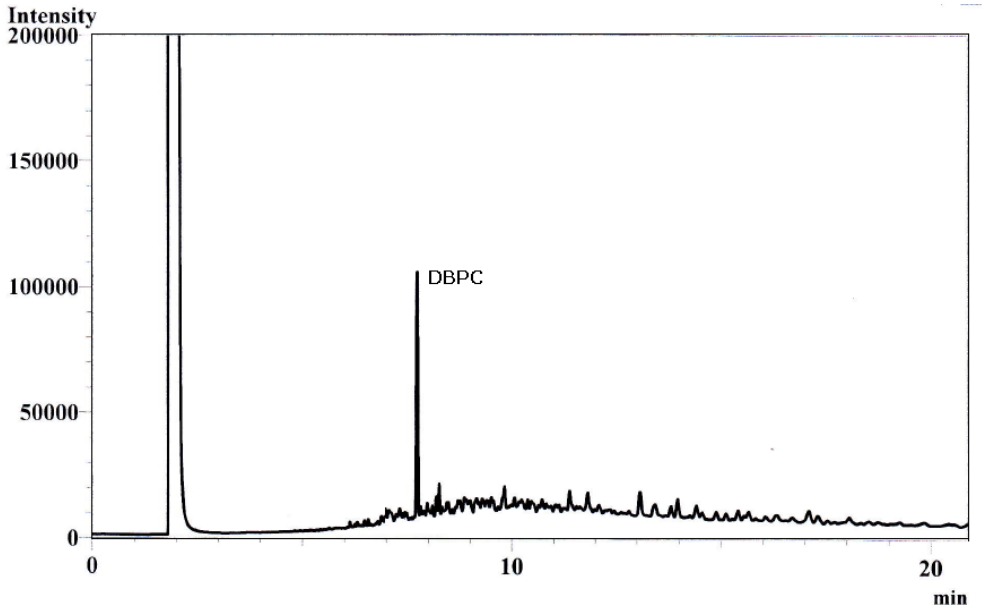


Fig 2.3. A Chromatogram for mineral oil containing 0.2% DBPC in oil diluted with n-hexane after extraction with acetonitrile using oil:n-hexane:acetonitrile ratio of 5:2:5 (v/v/v).

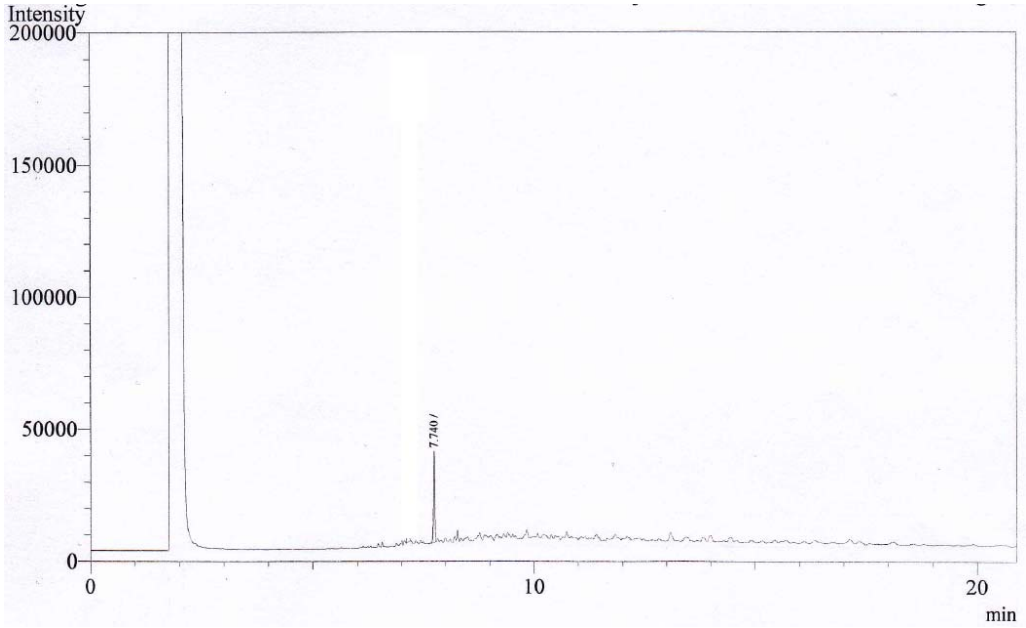


Fig 2.4. A chromatogram for mineral oil containing 0.2% DBPC in oil after solid phase extraction according to the ASTM D 4768.

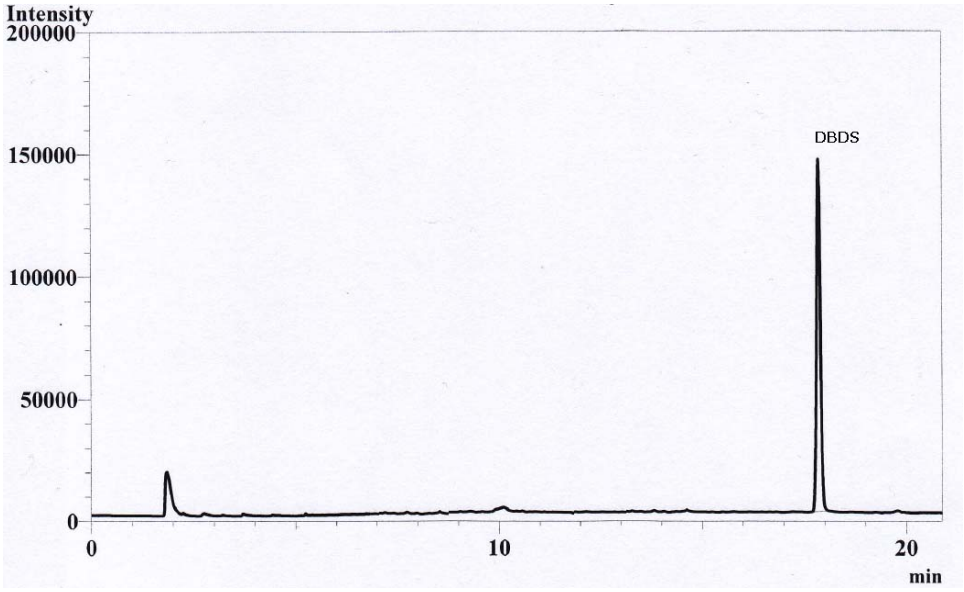


Fig 2.5. A chromatogram for insulating oil containing 50 mgL^{-1} DBDS diluted with n-hexane and extracted with acetonitrile using oil:n-hexane:acetonitrile ratio of 5:2:5 (v/v/v).

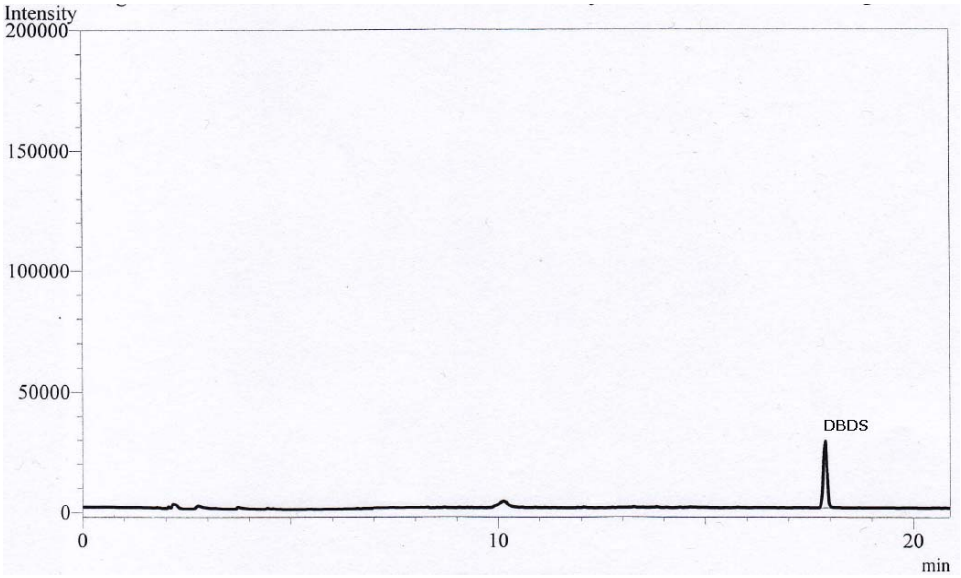


Fig 2.6. A chromatogram for insulating oil containing 50 mgL^{-1} DBDS determined by GC/ECD according to the IEC-62697 method.

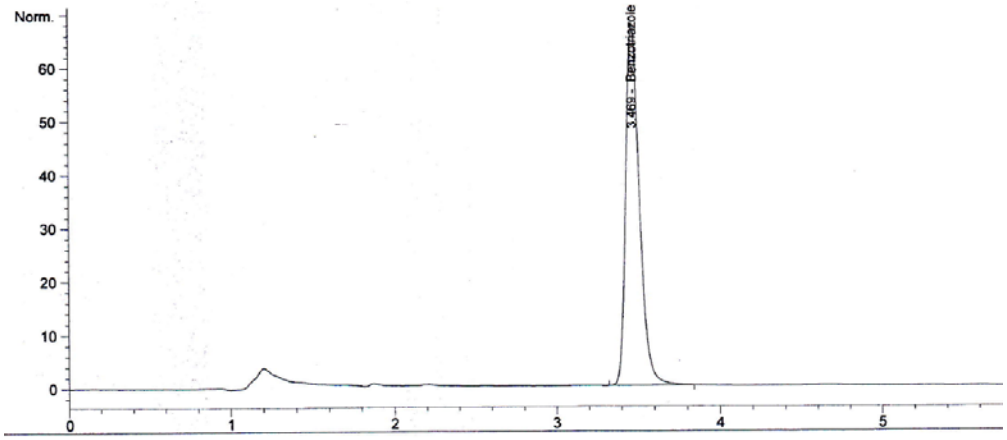


Fig 2.7. A chromatogram for insulating oil containing 50 mg.L^{-1} BTA diluted with n-hexane and extracted with acetonitrile using oil:n-hexane:acetontrile ratio of 5:2:5 (v/v/v).

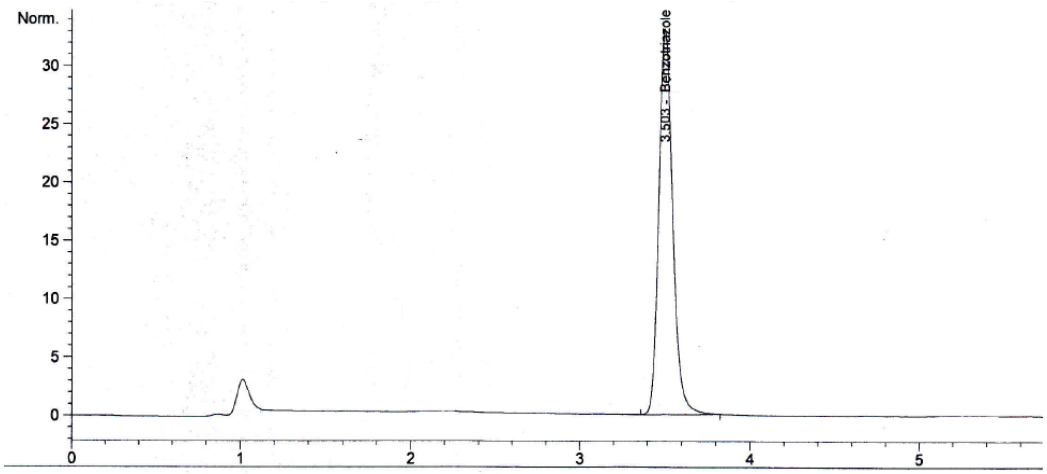


Fig 2.8. A chromatogram for insulating oil containing 50 $mg.L^{-1}$ BTA determined by the IEC-60666 HPLC method.

2.3.2 Further investigation on the liquid-liquid extraction pretreatment step

The DBPC signal in the GC-chromatogram, as observed in this work, was almost increased three times when liquid-liquid extraction was used as a pretreatment step for the extraction of 0.2% DBPC. The use of n-hexane in this liquid-liquid extraction pretreatment has decreased the possibility of the oil matrix extraction in the extractant (acetonitrile or methanol) phase. n-Hexane was used earlier as a diluent for edible oil samples when the synthetic phenolic antioxidants were extracted by acetonitrile polar solvent prior to their determination by micellar electrokinetic capillary chromatography [35]. The need for n-hexane as a co-solvent in the extraction was attributed to its role in decreasing the viscosity of the oil sample, a matter that enhances the contact between the oil/acetonitrile phases. When the same liquid-liquid extraction pretreatment step was carried out in the absence of n-hexane, the chromatogram showed a high background contribution (Fig. 2.9) indicating the presence of oil traces in the acetonitrile layer. However, when a sample of this acetonitrile layer was shaken with n-hexane (mineral oil: n-hexane; 5:2, v,v), a chromatogram similar to that of (Fig. 2.10) was obtained where the background has been almost disappeared. It is more likely that the nonpolar n-hexane solvent competes with the acetonitrile extractant for the oil matrix, thus it minimizes the oil extraction into the acetonitrile layer. The same argument was also valid when BTA was extracted by solid phase extraction or liquid-liquid extraction followed by injection into an HPLC system. The significant dilution of the oil sample prior to DBDS determination using the standard method IEC-62697 should be responsible for the low chromatographic peak sensitivity and consequently the high limit of detection reported there (≤ 5 mgL^{-1}) [29]. Figs. 2.11 and 2.12 show that the signal of 1 mgL^{-1} DBDS is an analytical challenge for the new proposed method of liquid – liquid pretreatment extraction step.

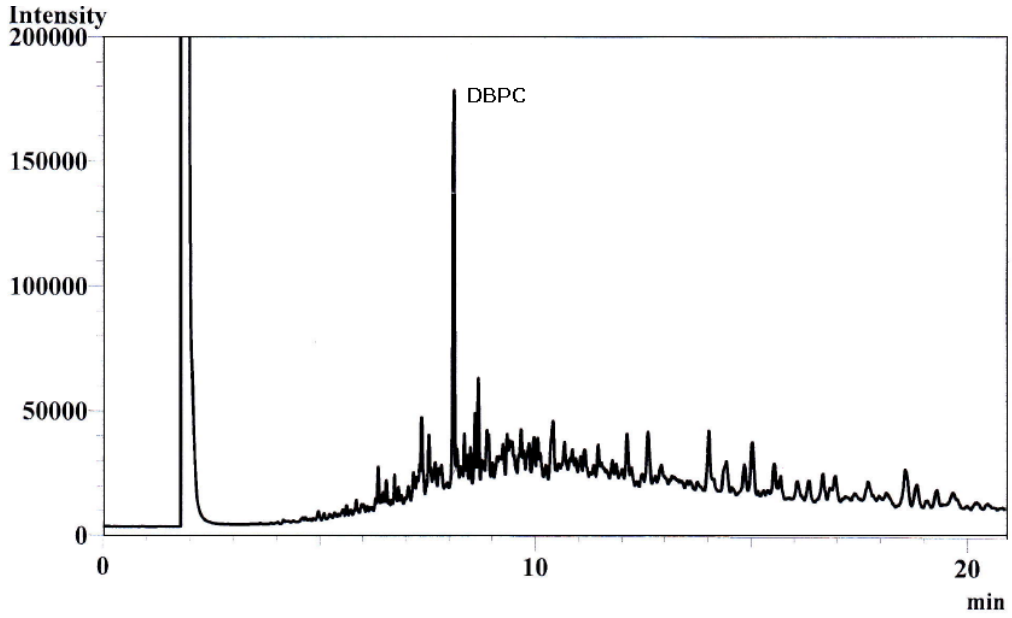


Fig 2.9. A chromatogram for a new mineral oil containing 0.2% DBPC only and extracted with acetonitrile.

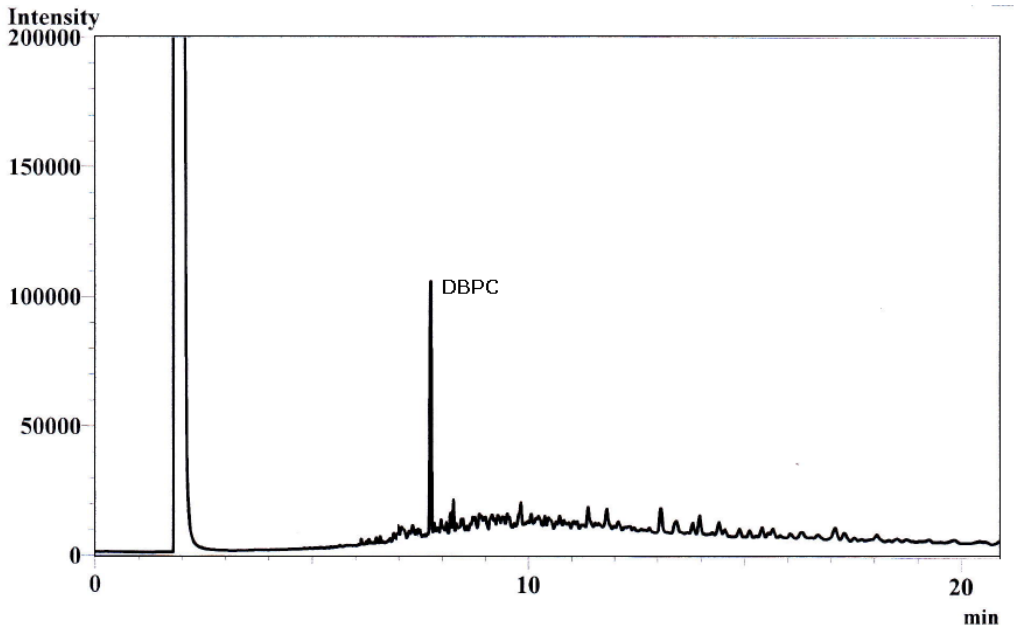


Fig 2.10. A chromatogram for insulating oil containing 0.2% DBPC diluted with n-hexane and extracted with acetonitrile using oil:n-hexane:acetonitrile ratio of 5:2:5 (v/v/v).

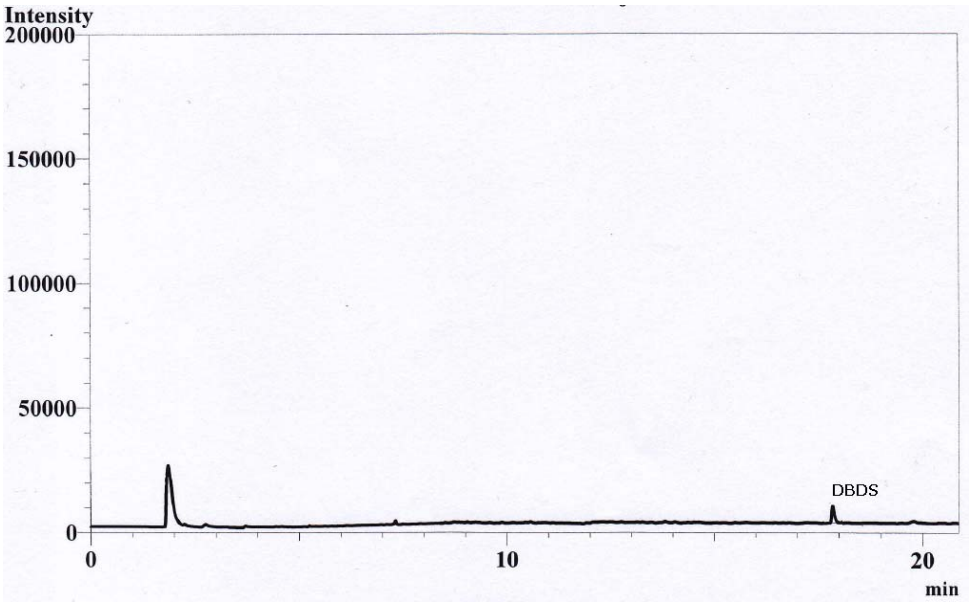


Fig 2.11. A chromatogram for mineral oil containing 1 mgL^{-1} DBDS diluted with n-hexane and extracted with acetonitrile using oil:n-hexane:acetonitrile ratio of 5:2:5 (v/v/v).

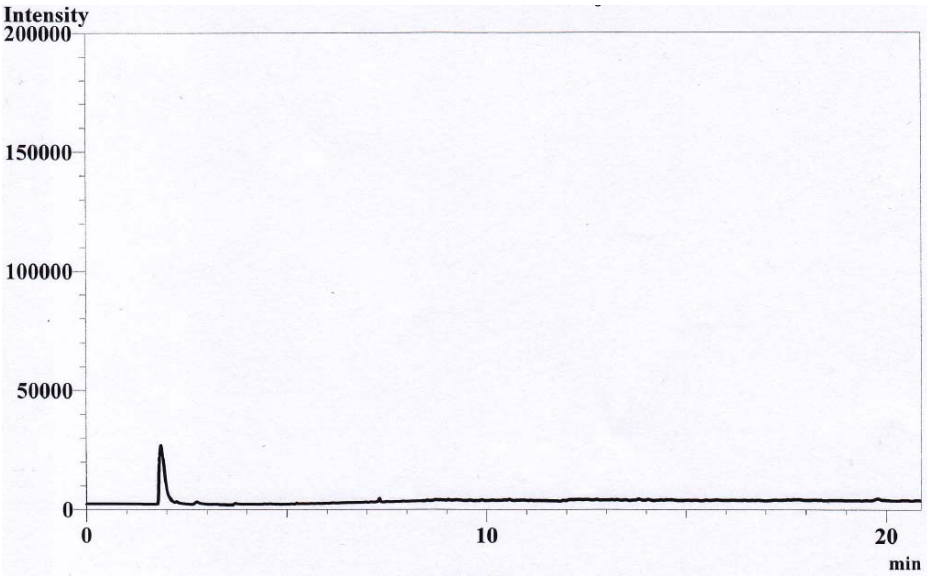


Fig 2.12 A chromatogram for mineral oil containing 1 mgL^{-1} DBDS diluted with acetonitrile and determined according to the IEC-62697 Standard method.

Because of the need for extensive dilution, IEC-62697 was not able to detect 1 mgL^{-1} DBDS signal and this agreed with the expected detection limit as estimated by the method (5 mgL^{-1} DBDS).

These investigations indicated that solid-phase extraction requires various elution steps that may dilute the analyte to be determined in the oil sample, thus decreasing the sensitivity and detection limit of the chromatographic signal may take place. Furthermore, appreciable quantities of solvents and time will be consumed compared to the liquid-liquid extraction pretreatment as described in this work. Consequently, the efficiency of liquid-liquid extraction protocol was assessed to optimize the volumes of the components that give the maximum chromatographic peak areas.

2.3.3 Optimizing of volume ratios in the liquid-liquid extraction process

The focus of this work was to introduce a single, easy and efficient liquid-liquid extraction step with minimal use of solvents where DBDS, DBPC and BTA are extracted simultaneously from the mineral oil matrix prior to their determination by GC and HPLC techniques. The extraction efficiency was assessed by varying the volume ratios: mineral oil/oil diluent/ extractant solvent until the optimum ratio that produced the highest GC/HPLC signal sensitivity was obtained; this would indicate the highest extraction efficiency. Two sets of mineral oil/oil diluent/ extractant solvent volume ratios were studied, where in one of them the extractant solvent was 5 ml acetonitrile while in the other it was 5 ml methanol. The components of each set were as follows: Y:X:5, where Y (mineral oil) = 2 or 5 ml, and X (n-hexane) = 2 or 5 ml. Thus 4 combinations were prepared for each extractant solvent. A series of solutions (a total of 4 solutions for each extractant solvent)

comprising various DBDS, DBPC and BTA concentrations (1 to 100 mgL^{-1} for DBDS and BTA and 0.01 to 1% w/v for DBPC) dissolved in fresh mineral oil (Y ml) were prepared from each combination. The liquid-liquid extraction was carried out according to the procedure mentioned above, and a portion of each extract (acetonitrile or methanol layer) was separated, diluted with the internal standard when needed and injected into the GC to determine DBDS, DBPC simultaneously where one line is passed into an electron capture detector, ECD, to determine DBDS while the other line is passed into a flame ionization detector, FID, to determine DBPC. Another portion of the extractant was injected into the HPLC to determine BTA. Furthermore, two more series of standard solutions were prepared comprising DBDS, DBPC and BTA with the same range of concentrations but dissolved in pure acetonitrile in one time and in methanol in the other. Again, a portion of each of these sample solutions was injected into the GC system and another portion was injected into the HPLC system. Calibration curves were constructed for each of the three components (DBDS, DBPC and BTA) in each of the 4 series. The extraction efficiency for each volume ratio was calculated as the ratio of the slope of its curve to the slope of the curve for the same component in the same extractant solvent. The extraction efficiencies (percent extraction) are presented in Fig. 2.13.

It is obvious from Fig. 2.13 that acetonitrile achieved better extraction efficiency than methanol for each of the three components in all volume ratios, and the difference in percent extractability was more pronounced with DBDS. This difference in extractability might be ascribed to the differences in solubility of each of the three components in methanol and acetonitrile thus, the significant difference in the case of DBDS might be attributed its higher

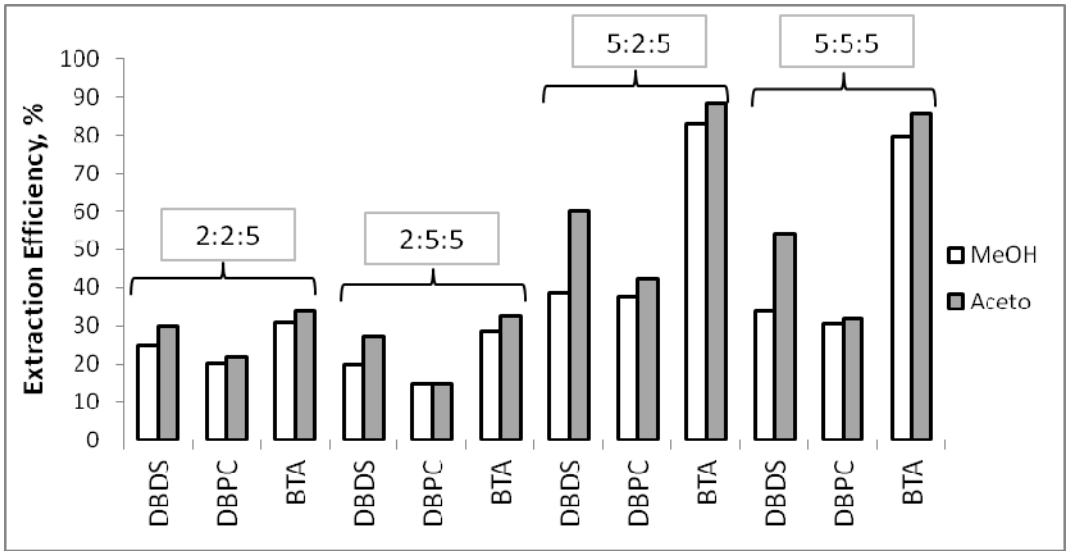


Fig 2.13. The extraction efficiencies for several volume ratios (mineral oil/oil diluents/extractant solvent) using acetonitrile and methanol.

solubility in acetonitrile compared to that in methanol. Increasing the volume of the oil diluent from 2 to 5 ml seems to have a little effect on the extraction efficiency except for DBPC. This increase caused a decrease in extraction efficiency for about 7-9% for DBPC in acetonitrile or methanol, however, the decrease in extraction efficiency for the others were ranging from about 2% to 3%. This decrease may be attributed to the competition of acetonitrile and n-hexane for each of the components. The dramatic increase in the extraction efficiency was observed when the volume of oil sample was increased from 2 to 5 ml. Fig. 2.13 shows that the highest extraction efficiencies for the three components was achieved when the mineral oil/oil diluent/extractant solvent was 5: 2: 5. Consequently, this volume ratio was recommended as the optimum for extraction prior to GC and HPLC determination of the components.

As Fig. 2.13 indicates, the optimum extraction efficiency did not reach 100% hence, in conducting such determinations, standards and oil sample solutions must have the same pretreatment before injecting into the GC-ECD-FID and HPLC systems in order to compensate for the difference in the extractability.

2.3.4 Linearity, sensitivity and limit of detection for the GC and HPLC calibration curves

The linearity was established for concentration ranges of 0.01 -1.00 % w/v DBPC, 1 - 100 $mg.L^{-1}$ DBDS and 1 - 100 $mg.L^{-1}$ BTA solutions prepared in fresh mineral insulating oil and extracted by acetonitrile liquid-liquid extraction using the optimum volume ratio followed by injection into the GC-ECD/FID and HPLC/UV systems under the optimum operational

and instrumental conditions [29, 31 and 38]. Diphenoxy benzene and diphenyl disulfide internal standards were used with DBPC and DBDS, respectively, whereas BTA calibration curve was established using external standard method. Though the HPLC-UV detector is recommended to be set at 260-270 nm to measure the absorbance of BTA according to the standard method, IEC-60666 [38], it has been set here at 250 nm, especially with used oil to almost eliminate the chromatographic interference of certain oxidation byproducts (furanic compounds such as 2-furaldehyde) that form in the oil as a result of oil and insulating paper degradation and overheating. The maximum absorbance wavelength for this furanic compound is expected to be in the range of 272-280 nm [40], however, the wavelength of maximum absorbance for BTA is at 260 nm (Fig. 2.14). The measurement at 250 nm gave significant signal sensitivity for BTA and a minimal absorbance for the furanic compounds. Thus, there was no need for the standard addition method as proposed by the IEC-60666 [38] when dealing with used oil.

Table 2.3 shows the linearity, slope and limit of detection determined according to Millar and Millar [41] of GC and HPLC calibration graphs for DBPC, DBDS and BTA following the liquid-liquid extraction pretreatment described above and the literature standard methods in which the pretreatment was only a dilution by isooctane as in the case of DBDS or solid phase extraction as in the case of DBPC and BTA [31, 38]. As appears from Table 2.3 and (Figs. 2.15- 2.17), the slopes of calibration curves that reflect their sensitivities are much higher for this work and the detection limits are much lower compared with those of the standard methods. This sensitivity enhancement may be ascribed to the type of column and eluent used.

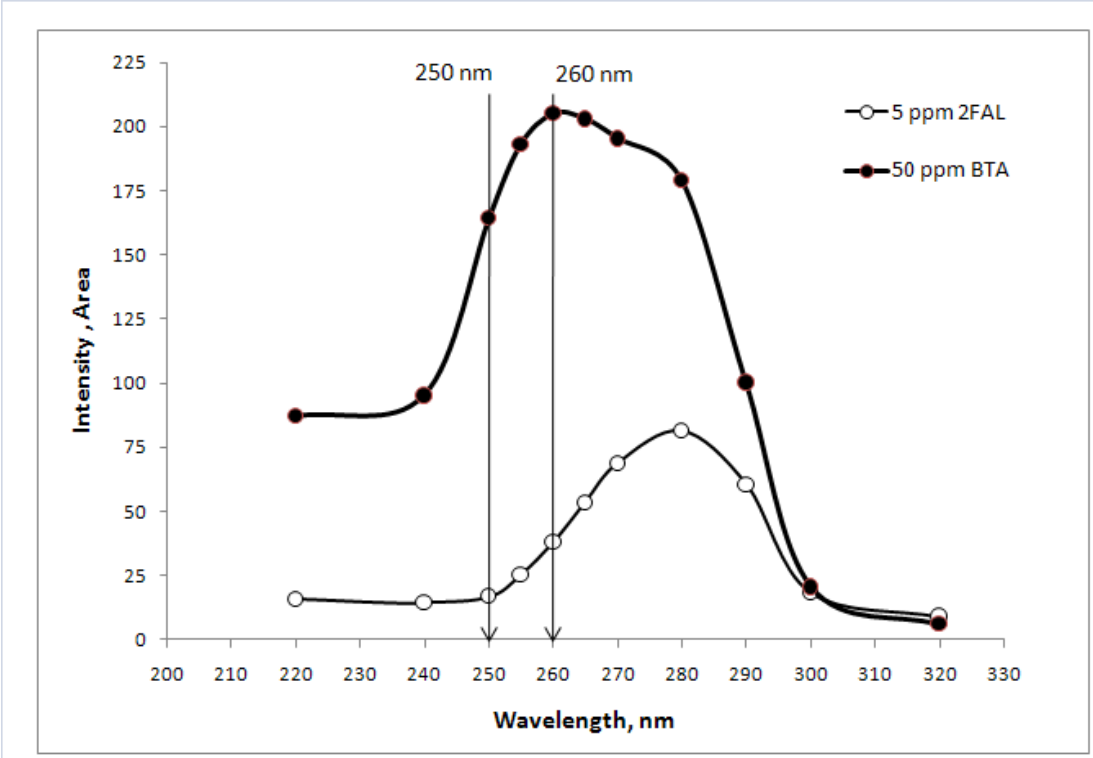


Fig. 2.14. Wavelength selection criteria for BTA when furanic compounds are present in the mineral oil matrix.

Table 2.3 Linearity, slope and limit of detection of calibration graphs for DBPC, DBDS and BTA using the liquid-liquid extraction described here and the literature standard methods

Regression	DBPC		DBDS		BTA	
Parameter	ASTM D 4768	Liquid – Liquid Ext.	IEC-62697	Liquid – Liquid Ext.	IEC-60666	Liquid – Liquid Ext.
R^{2} [a]	0.995	0.999	0.999	0.997	0.997	0.999
Slope [a]	0.81 ± 0.01	1.84 ± 0.04	0.01 ± 0.00	0.04 ± 0.00	2.53 ± 0.23	5.03 ± 0.21
LOD [b]	0.05 % w/v	0.01 % w/v	1.80 mgL^{-1}	0.80 mgL^{-1}	5.30 mgL^{-1}	2.04 mgL^{-1}

a) Calibration ranges: 0.01 – 1.00 % w/v DBPC and 1 – 50 mgL^{-1} DBDS / BTA

b) Calibration ranges: 0.01 – 0.50 % w/v DBPC and 1 – 50 mgL^{-1} DBDS / BTA

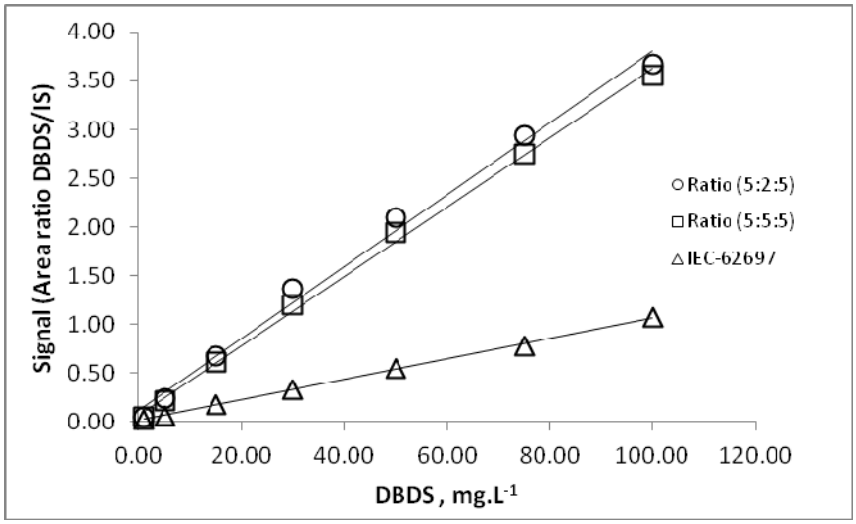


Fig 2.15. Calibration curves for DBDS in mineral oil using the reference method and the liquid – liquid extraction pretreatment step followed by the GC/ECD determination method where the oil:n-hexane:acetonitrile ratios were 5:2:5 and 5:5:5 (v/v/v).

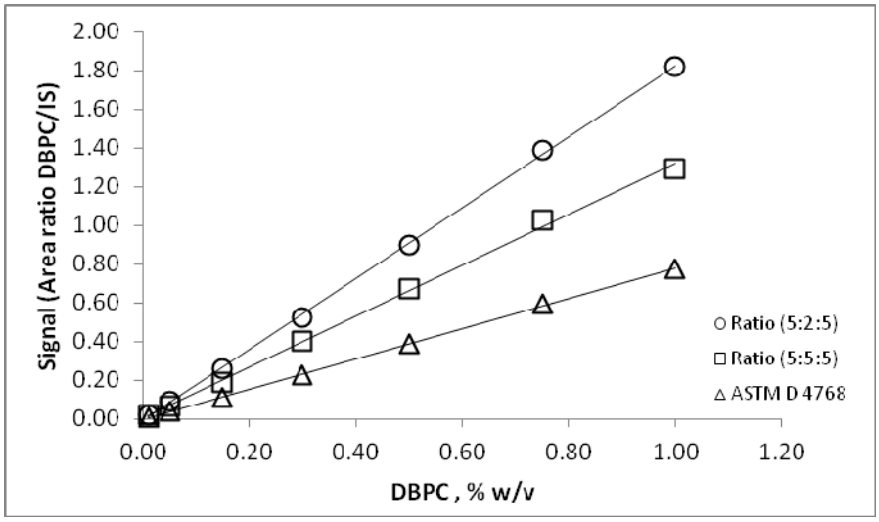


Fig 2.16. Calibration curves for DBPC in mineral oil using the reference method and the liquid – liquid extraction pretreatment step followed by the GC/FID determination method where the oil:n-hexane:acetonitrile ratios were 5:2:5 and 5:5:5 (v/v/v).

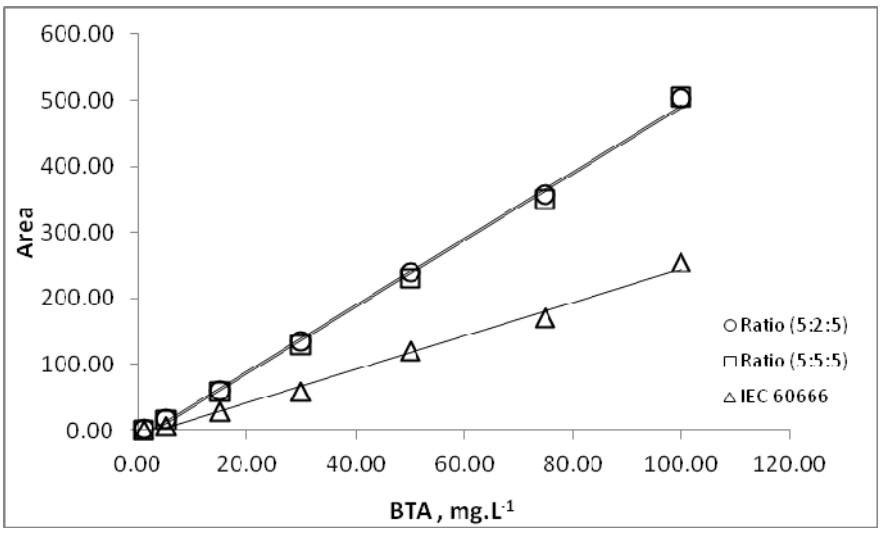


Fig 2.17. Calibration curves for BTA in mineral oil using the reference method and the liquid – liquid extraction pretreatment step followed by the HPLC/UV determination method where the oil:n-hexane:acetonitrile ratios were 5:2:5 and 5:5:5 (v/v/v).

According to the standard method IEC 62697 [29], a significant interference of polychlorinated biphenyles, PCB, with DBDS signal was observed. However, this interference was completely removed when the DB-5 column was used under the same conditions and using same ECD detector. Figs 2.18 and 2.19 demonstrate two chromatograms for 10 mgL^{-1} DBDS mixed with 1 mgL^{-1} PCB in acetonitrile solvent and injected in DB-5 column and the recommended column by IEC 62697 (RTX-5). Although DBDS signal was more prominent through RTX-5, PCB signal indicated an interference with DBDS signal with a critical overlapping. This interference has disappeared when the same solution was injected to DB-5 column under the same conditions used in RTX-5.

2.3.5 Accuracy, precision and signal stability of GC and HPLC determinations

Accuracy and precision of the determinations of DBPC, DBDS and BTA in mineral oil using GC and HPLC techniques preceded by liquid–liquid extraction pretreatment on one hand and the standard methods on the other hand have been estimated for fresh and aged samples. The results are presented in Tables 2.4 (DBDS), 2.5 (DBPC) and 2.6 (BTA). The percent recoveries for DBDS were in the range of 98.9% to 102.3% with %RSD's of 0.45 to 6.28 for various DBDS concentration ranges (1-150 mgL^{-1} DBDS). The two-sided ***t*** test was used to investigate whether the means differ significantly from zero. Student's ***t*** values for three replicates of measurements made on each sample at 95% confidence level, indicated that no significant difference existed between the experimental means obtained from this GC-ECD following the liquid-liquid extraction pretreatment and the IEC-62697 standard method (Table 2.4).

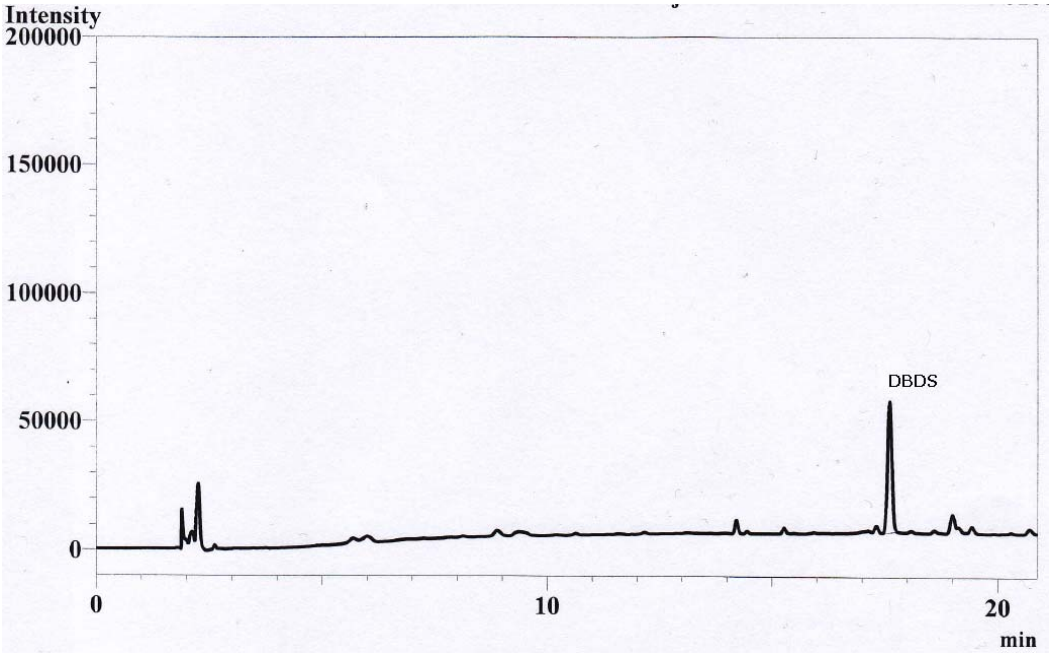


Fig. 2.18. A GC/ECD chromatogram for 1 mgL^{-1} PCB, and 10 mgL^{-1} DBDS dissolved in pure acetonitrile using DB-5 column.

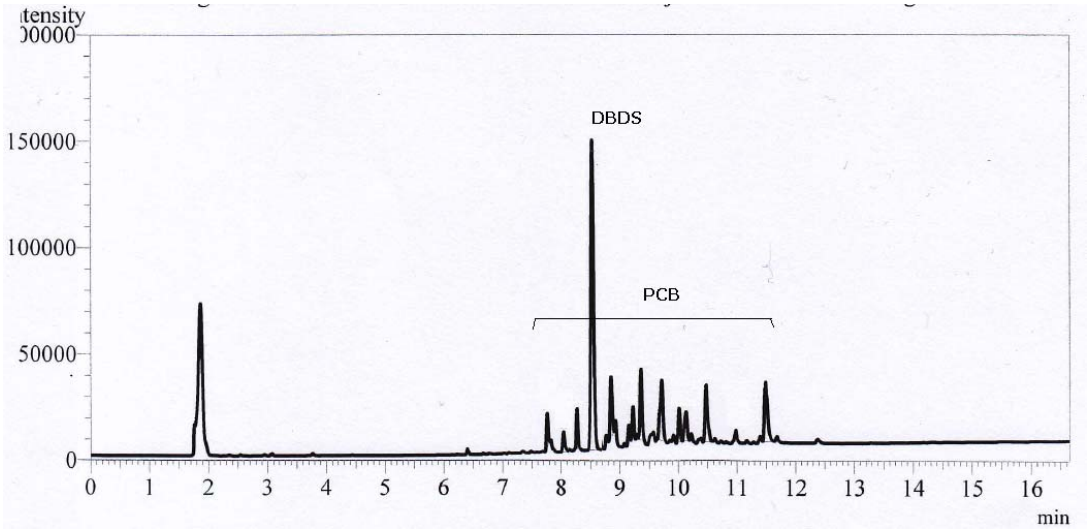


Fig 2.19. A GC/ECD chromatogram for 1 mgL^{-1} PCB, and 10 mgL^{-1} DBDS dissolved in pure acetonitrile using the recommended column as per IEC-62697 method.

Table 2.4: Accuracy and precision for DBDS determination in insulating oils using various methods.

Qty Added DBDS (mgL^{-1})	Liquid-Liquid Extraction Acetonitrile (5 : 2 : 5)		IEC-62697		ASTM D1275 B	*t* student test two-sided	ASTM D 130 [a]
	Qty Found DBDS (mgL^{-1})	Recovery (%)	Qty Found DBDS (mgL^{-1})	Recovery (%)	Corrosive – Noncorrosive	(n = 3)	
1.00	1.02	102.33	Not Detected	-	None Corrosive	-	Degree of corrosion is 1a
%RSD	6.28		-				
10.00	10.07	100.7	10.33	103.27	None Corrosive	1.24	Degree of corrosion is 1b
%RSD	1.84		2.99				
20.00	20.33	101.67	19.66	98.30	None Corrosive	2.90	Degree of corrosion is 3b
%RSD	0.85		1.85				
50.00	49.93	99.86	50.44	100.87	Corrosive	1.74	Degree of corrosion is 4a
%RSD	0.61		0.79				
100.00	99.27	99.27	99.99	99.99	Corrosive	1.98	Degree of corrosion is 4b
%RSD	0.63		0.11				
150.00 [b]	148.32	98.88	149.58	99.72	None Corrosive	2.56	Degree of corrosion is 1b
%RSD	0.45		0.36				

a. Qualitative visual corrosion classification as per ASTM D 130

b. The oil sample was passivated with 30 mgL^{-1} 1,2,3-benzotriazole

Table 2.5: Accuracy and precision for DBPC determination in insulating oils using various methods.

Qty Added DBPC (% w/v)	Liquid-Liquid Extraction Acetonitrile (5 : 2 : 5)		ASTM D 4768		*t* student test two-sided (n = 3)
	Qty Found DBPC (% w/v)	Recovery (%)	Qty Found DBPC (% w/v)	Recovery (%)	
0.01	0.011	110.0	Not Detected	-	-
%RSD	5.41		-		
0.05	0.051	97.0	0.052	104.0	0.46
%RSD	2.97		3.85		
0.10	0.101	101.0	0.102	102.0	0.36
%RSD	4.48		6.51		
0.20	0.204	102.0	0.209	104.7	0.57
%RSD	4.16		5.26		
0.30	0.296	98.8	0.304	101.3	2.14
%RSD	0.51		1.97		
0.30 [b]	0.301	100.3	0.308	102.8	2.63
%RSD	0.99		1.23		

a. 0.30% w/v DBPC spiked in aged oil matrix

Table 2.6: Accuracy and precision for 1,2,3-Benzotriazole determination in insulating oils using various methods.

Qty Added BTA (mgL^{-1})	Liquid-Liquid Extraction Acetonitrile (5 : 2 : 5)		IEC-60666		ASTM D1275 B	*t* student test two-sided (n = 3)	ASTM D 130 [a]
	Qty Found BTA (mgL^{-1})	Recovery (%)	Qty Found BTA (mgL^{-1})	Recovery (%)	Corrosive – Noncorrosive		
2.00 [b]	2.08	104.17	Not Detected	-	Corrosive	-	Degree of corrosion is 4a
%RSD	1.69		-				
10.00 [b]	9.99	99.87	10.04	100.4	None Corrosive	0.77	Degree of corrosion is 3b
%RSD	0.80		0.89				
30.00 [b]	30.03	100.09	29.91	99.69	None Corrosive	0.51	Degree of corrosion is 2b
%RSD	0.36		1.32				
50.00 [b]	50.25	100.51	49.95	99.90	None Corrosive	1.38	Degree of corrosion is 1a
%RSD	0.57		0.50				
50.00 [c, b]	50.02	100.03	49.38	98.76	None Corrosive	3.06	Degree of corrosion is 1b
%RSD	0.29		0.67				
100.00 [c]	100.01	100.01	98.76	98.76	-	4.16	-
%RSD	0.18		0.50				

a. Qualitative visual corrosion classification as per ASTM D 130

b. The oil sample was spiked with 50 mgL^{-1} DBDS

c. Aged oil matrix contained 1000 μgL^{-1} 2-furaldehyde

Table 2.4 shows also that the IEC-62697 standard method did not detect DBDS at 1 mgL^{-1} level. This may be ascribed to the need for an oil sample dilution of about 20 times to facilitate its elution through the GC column. The ASTM D1275 B did not detect the presence of DBDS even at concentration of about 20 mgL^{-1} DBDS. Furthermore, when an oil sample containing DBDS as high as 150 mgL^{-1} was passivated with 30 mgL^{-1} BTA, ASTM D 1275 gave a result of non-corrosivity of the oil, a conclusion that gives a false indication to the presence of DBDS. The percent recoveries for DBPC were in the range of 98% to 110% for concentration ranges of 0.01% to 0.30% (w/v). Student's *t* values indicated no significant difference existed between the experimental means obtained from this GC-FID following the liquid-liquid extraction pretreatment and the ASTM D 4768 standard method (Table 2.5). It is obvious from Table 2.5 that 0.01% (w/v) DBPC was not detectable when the standard method was used.

The percent recoveries for BTA were in the range of 99.9% to 104.2% for concentration ranges of 2-100 mgL^{-1} BTA. Student's *t* values indicated no significant difference existed between the experimental means obtained from this HPLC/UV method following the liquid-liquid extraction pretreatment and the IEC-60666 standard method (Table 2.6). The percent recovery was about 100% when the liquid-liquid extraction pretreatment for an aged oil sample containing 100 mgL^{-1} BTA and spiked with 1000 μgL^{-1} 2-furaldehyde was tested (Table 2.6). The method is accurate and precise and can be used successfully for different mineral insulating oil matrices used for transformers. Consequently, the liquid-liquid extraction pretreatment facilitates the removal of the oil matrix, pre-concentrate the analyte (DBDS, DBPC and BTA), reduces the analysis time of the three components that may need

to be tested together to judge the quality and characteristics of the mineral insulating oil when fresh or used. Thus, DBDS, the antioxidant and corrosive component at the same time can be detected and controlled even at concentrations as low as 1 mgL^{-1} and in the presence of the BTA passivator. These findings would help studying the kinetics of copper corrosion in the transformer where the concentrations of DBDS, DBPC and BTA should be smaller than the levels detected by the standard methods, a study that is currently under investigation.

The signal stability was tested statistically using Shewhart control chart method. 15 oil samples of 10 mgL^{-1} DBDS, 30 mgL^{-1} BTA and 0.15% w/v DBPC were tested by GC and HPLC techniques preceded by liquid–liquid extraction pretreatment at different time intervals (about 40 min and 10 min between each run for DBDS/DBPC and BTA respectively). The interpretation of the control chart (Figs. 2.20-2.22) indicated that the method is

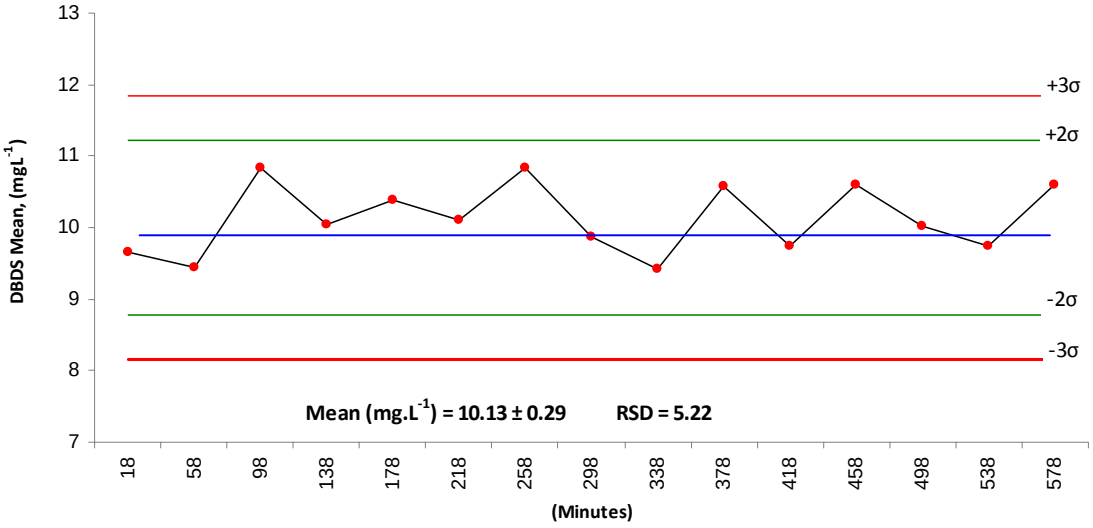


Fig. 2.20. Long term signal stability for 10 mgL^{-1} DBDS extracted from mineral insulating oil by acetonitrile liquid – liquid followed by GC-ECD detection.

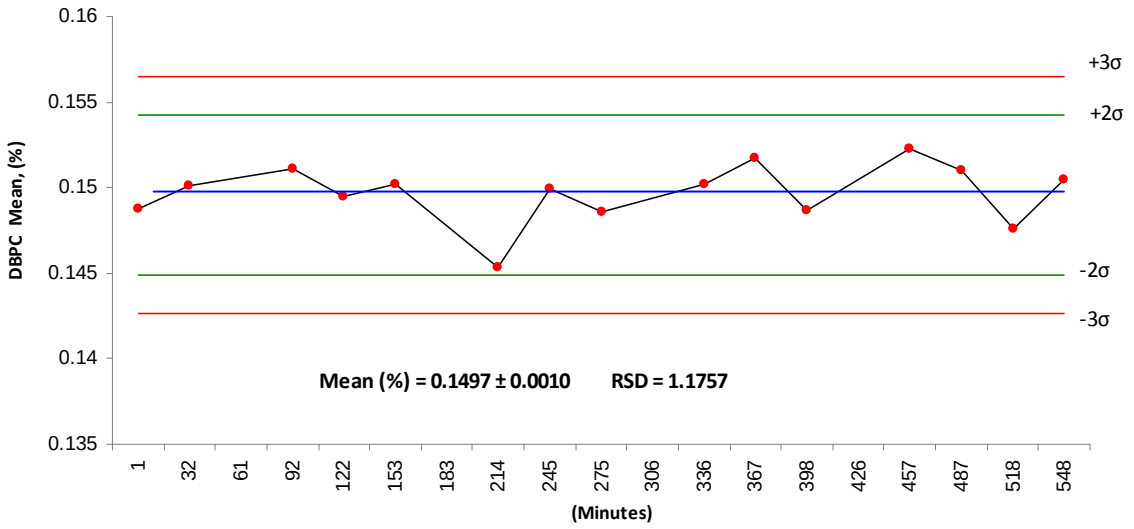


Fig. 2.21. Long term signal stability for 0.15% w/v DBPC extracted from mineral insulating oil by acetonitrile liquid – liquid followed by GC-FID detection.

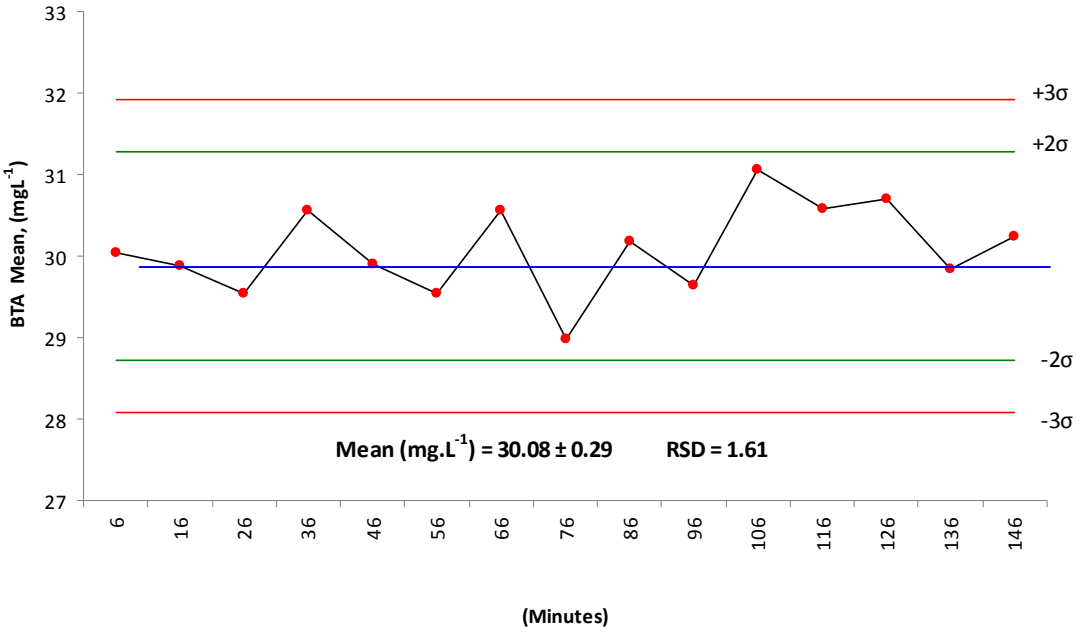


Fig. 2.22. Long term signal stability for 30 mgL^{-1} BTA extracted from mineral insulating oil by acetonitrile liquid – liquid followed by HPLC-UV detection.

statistically under control with confidence limits calculated at 95% of 10.13 ± 0.29, 0.1597 ± 0.0010 and 30.08 ± 0.27 and RSDs of 5.22, 1.172 and 1.610 for DBDS, DBPC and BTA respectively.

The adopted acetonitrile liquid – liquid extraction method was validated against each standard methods [29, 31, 38] using two methods of the regression line technique [41]. Acetonitrile liquid – liquid extraction method data have been plotted on x-axis and the related standard method results on y-axis (Figs. 2.23 - 2.25). The output shows that the R value for each component is better than 0.999 which indicates to an acceptable correlation between the adopted acetonitrile liquid – liquid extraction method and the standard methods used for each component. The slope and intercept values were calculated for each species in the basis of 95% confidence limit where the upper and lower confidence limits include the values 1 and 0, respectively, indicating to acceptable correlation between acetonitrile liquid – liquid extraction method and the tested standard methods.

2.4 Conclusion

This work describes an efficient single and fast pretreatment method for fresh and used transformer oil samples in which a minimal consumption of solvents is used for simultaneously liquid-liquid extraction of three important additives of the mineral oil, namely, DBDS, DPBC and BTA in order to facilitate their determination by GC and HPLC techniques. DBDS and DBPC are determined simultaneously by GC/ECD/FID technique while BTA is determined by an HPLC technique.

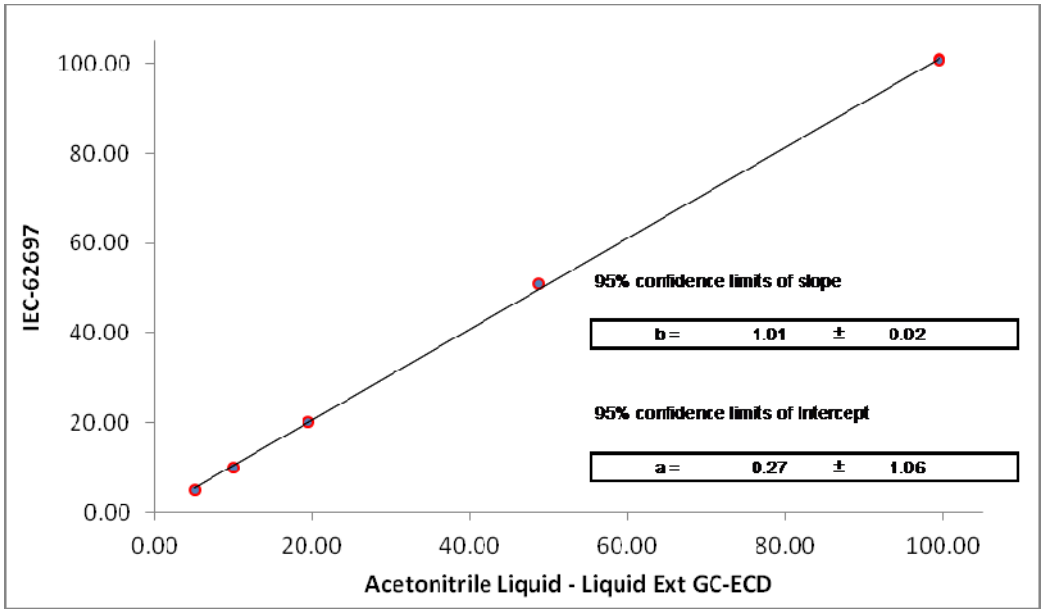


Fig 2.23. The regression line for acetonitrile liquid – liquid extraction GC-ECD and IEC-62697 methods to quantify several DBDS concnetrations in mineral insulaitng oil.

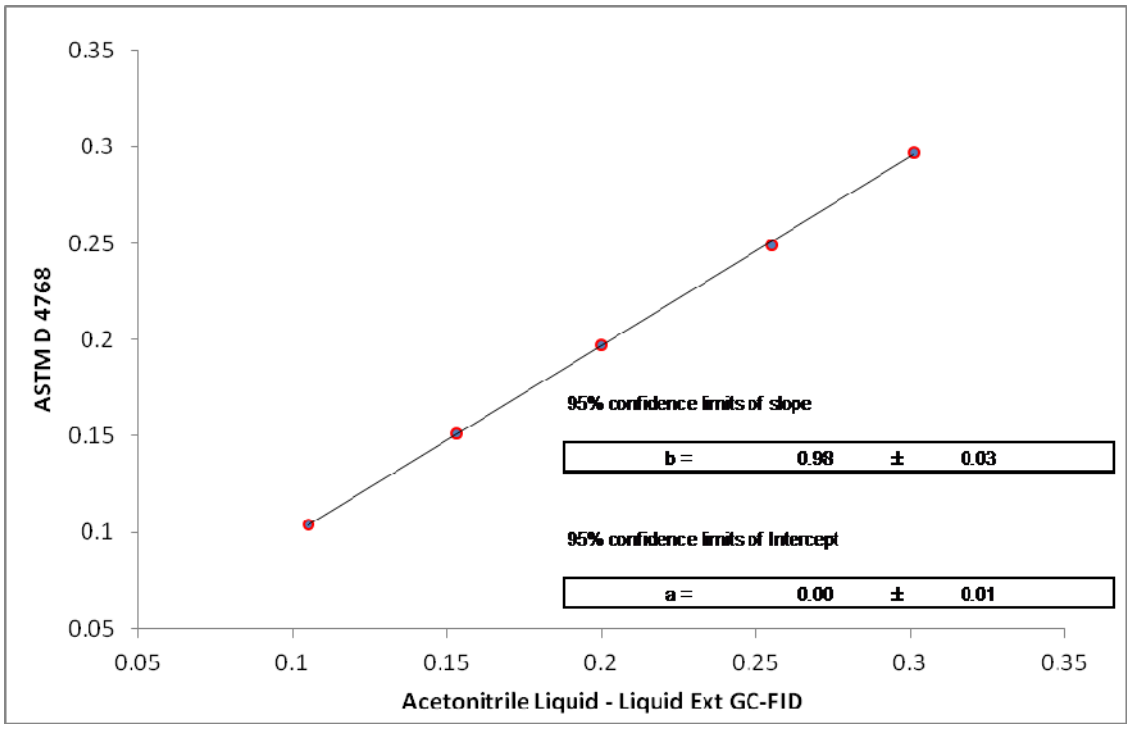


Fig 2.24. The regrission line for acetonitrile liquid – liquid extraction GC-FID and ASTM D 4768 methods to quantify several DBPC concnetrations in mineral insulaitng oil.

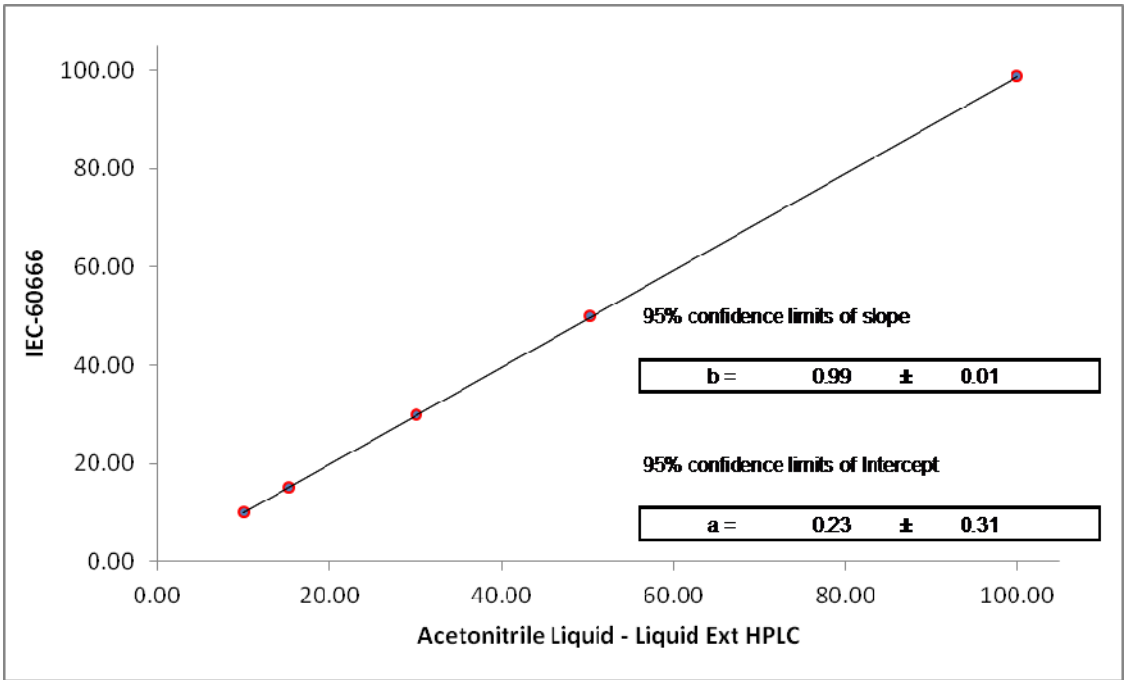


Fig 2.25. The regrission line for acetonitrile liquid – liquid extraction HPLC-UV and IEC-60666 methods to quantify several BTA concnetrations in mineral insulaitng oil.

Comparison of the results of this method for each of the three components to those obtained by the standard methods, revealed that this method provides better sensitivity and lower detection limits as a result of the pre-concentration and removal of the mineral oil matrix that may interfere with the determination of the components. Determining relatively low concentrations of these three components would help studying their interaction effects in the mineral oil and its corrosion and passivation actions under the transformer operational conditions. Traditionally this interaction effect is studied indirectly by investigating the copper sulfide formation. This matter is currently under investigation.

Chapter Three

Determination of the threshold concentration of DBDS in mineral insulating oils

3.1 Introduction

It was reported [9, 10] that there is a critical concentration of DBDS below which this compound will not act as a corrosive species in the mineral oil matrix. This concentration is under investigation and still considered as a matter of confusion in the literature. The following reaction represents the role of DBDS existing in the mineral insulating oil matrix when its concentration and the temperature inside the transformer unit are optimum for the formation of Cu_2S. [9, 20].

$$4Cu + C_6H_5\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2\text{-}C_6H_5 \xrightarrow{\triangle} 2Cu_2S\downarrow + C_6H_5\text{-}CH_2\text{-}CH_2\text{-}C_6H_5$$

Many approaches were conducted and used to determine the DBDS threshold concentration. Standard methods like ASTM D 1275 and IEC 62535 were utilized to visualize the corrosion level on copper strips when different amounts of DBDS were added to the mineral oil matrix.

Maina et al [10] used insulating oil samples containing 50 mgL^{-1} DBDS to investigate the corrosion effect using the ASTM D 1275-A method. The DBDS concentrations in the oil were determined by a gas chromatograph system equipped with an atomic emission detector (GC-

AED) before and after the test. This analysis showed that DBDS concentrations decreased significantly in the oil samples until the DBDS concentration fell below 10 mgL^{-1} at which copper corrosion was not observed. Another experiment similar to the ASTM D 1275 method was conducted by the same author where 20 ml headspace vials were separately filled with mineral oil containing different concentrations of DBDS in presence of small copper strips in each vial. The copper corrosion was observed in vials having DBDS concentrations above 20 mgL^{-1}. Commercially available naphthenic oil "free of DBDS" which is non corrosive, has exhibited corrosive behavior when it was spiked with DBDS at values greater than 50 mgL^{-1}[10].

Maina et al [12] stated that DBDS is present in approximately 90% of the insulating oils employed within the European market. Considering 20 mgL^{-1} of DBDS as a threshold to commence oil corrosive, it was found that 89.7% of a sample of 242 oils would derive their corrosiveness from DBDS. Most of the investigations on the corrosiveness of mineral insulating oils have been related to the presence of DBDS in them.

Maria et al [13] conducted a study to find the minimum effective DBDS concentration in mineral oil that makes it potentially corrosive. In this study, the IEC 62535 method was applied to investigate several DBDS concentrations in the range of 148 to 7 mgL^{-1} DBDS in mineral oil samples. This study concluded that a visible copper corrosiveness was observed at DBDS concentrations that are equal or greater than 10 mgL^{-1}. Therefore, a concentration of 10 mgL^{-1} of DBDS was considered to be the minimum amount necessary to make DBDS potentially corrosive.

Oil depolarization [12] is a procedure used for the removal of corrosive sulfur and other oxidation polar by-products from the oil matrix. A combination of solid reagents, chemicals and sorbents is used to filter the undesirable by-products in oil matrix including DBDS. In spite of the number of the treatment cycles and the high cost, depolarization does not reduce DBDS content to a level below 5 mgL^{-1}. The important issue here is that the critical concentration of DBDS is still not decided to confirm the usefulness of the depolarization treatment.

Most of the failures reported in the transformers are attributed to DBDS and they generally occur when the unit is operated at elevated temperatures. Thus, temperature is considered to be one of the key factors for this phenomenon. However, there has not been enough data to decide on the critical operation temperature. Amimoto et al [17] identified the temperature dependence of copper sulfide formation due to DBDS presence in mineral insulating oils. Copper deposition rate was tested at three different temperatures, 120° C, 130° C and 140° C and it was found that the deposition rate has doubled as the temperature was increased by 10° C.

In this study, the critical DBDS concentration and the temperature required for copper sulfide deposition were kinetically determined using the acetonitrile liquid – liquid extraction method. Instead of visually observing the corrosion on copper strips, the reaction rate for DBDS signal was investigated using several concentrations that are close to the reported [13] critical concentration of DBDS.

3.2 Experimental and methods

3.2.1 Procedure for the determination of the threshold concentration of DBDS

The determination of the DBDS threshold concentration was based on a quantitative measurement of the depletion rate of DBDS in mineral oil samples rather than the qualitative conclusions that depend on the visibility of copper corrosion according to IEC 62535 and ASTM 1275. Thus, various mineral oil samples (15 ml each) containing varying DBDS concentrations (3, 6, 9, 12 and 15 mgL^{-1} of DBDS) were stored in 20 ml glass headspace vials under sealed conditions. Identical copper strips were covered with Kraft insulating paper and immersed in each mineral oil solution. The vials were incubated at a temperature of 150° C and different time intervals of 1 to 168 hours.

This experiment was designed to measure the depletion of DBDS during different incubation intervals under constant thermal conditions. To differentiate between the corrosive behavior of DBDS and its behavior as an antioxidant, the experiment was conducted in presence and absence of copper strips. In both cases the same experimental conditions were applied.

To alleviate the effect of the dissolved oxygen, all mineral oil sample solutions were kept in a headspace oven at a temperature of 70° C and shaked for 30 minutes. Finally, while hot the samples were purged with argon for about one minute to reduce the dissolved oxygen content. It was found that dissolved oxygen in the tested insulating oil matrix was about 16,000 mgL^{-1} before purging. After purging all oil solutions with argon, the dissolved oxygen was reduced to a level of less than 2,000 mgL^{-1}. The oxygen content was determined by the standard ASTM D

3612 method. The vials were isolated from the atmospheric oxygen by covering them tightly with aluminum caps during the experiment. The time intervals for incubation were 1, 24, 48, 72, 96, 120, 144 and 168 hrs.

The DBDS depletion was quantitatively determined according to the method proposed in Chapter 2 where each oil sample solution was diluted with n-hexane and pretreated by acetonitrile liquid – liquid extraction followed by GC-ECD method.

3.2.2 Procedure for determination of critical temperature for copper sulfide formation

The same experimental conditions which were used for the determination of critical DBDS concentration were performed to estimate the critical temperature required for copper sulfide to start forming. Several solutions with a fixed DBDS concentration of 150 mgL^{-1} were prepared in mineral insulating oil matrix and subjected to incubation criteria same as that of the IEC-62535 method at different temperatures, namely, 50° C, 75° C, 100° C, 125° C and 150 ° C for time intervals of 1 to 120 hours.

3.3 Results and discussion

3.3.1 DBDS corrosive threshold concentration

This experiment was designed to determine quantitatively the threshold concentration of DBDS at 150 ° C. According to the work of other researchers a quantity of 10 mgL^{-1} of DBDS was estimated [13] as the threshold concentration at 150 ° C. As per the mechanism described by Toyama et al [20], above this concentration the corrosion cycle starts. The depletion rate of DBDS acting as a corrosive agent was calculated and used as an indicator for the level of

corrosion rather than observing the corrosion on copper strips visually. The extent of the depletion was studied for different incubation time intervals for various mineral oil samples containing different DBDS concentrations. Then, the observed depletion rate constants, k_{obs} , were drawn as a function of DBDS concentration [52] in order to determine if there is a sudden change in the rate that indicates a threshold concentration.

It is reasonable to assume that the reduction of dissolved oxygen in all the oil samples by purging with argon made the depletion of DBDS via its reaction as an antioxidant negligible. The results of this study are presented in Figs. 3.1-3.5. Therefore, all depletion results obtained belong only to the copper corrosion due to the DBDS. Table 3.1 illustrates the depletion of different initial concentrations of DBDS in mineral oil matrix kept at 150° C in contact with copper strips covered with insulating Kraft paper for different incubation times in hours. Fig. 3.6 represents a plot of DBDS concentration versus time of the decomposition of DBDS acting as a corrosive agent for copper strips immersed in the oil at various incubation periods. It is obvious that the DBDS decomposition takes place at all the initial concentrations studied starting from 3 mgL^{-1} until 15 mgL^{-1} (Figs 3.1 – 3.5). Thus, when added to the mineral oil DBDS will act as a corrosive agent even at concentrations that are less than 3 mgL^{-1}, since the corrosion activity at this concentration level was significantly detected.

When $Ln([A]/[A]_o)$ was drawn versus the incubation time, t (hours), the relationship is consistent with a first order reaction type, where, $[A]_o$ and $[A]$ represent the initial and the final DBDS concentration before and after the incubation period. For a first order reaction, $Ln([A]/[A]_o) = -kt$, where k is the observed reaction rate constant and t is time.

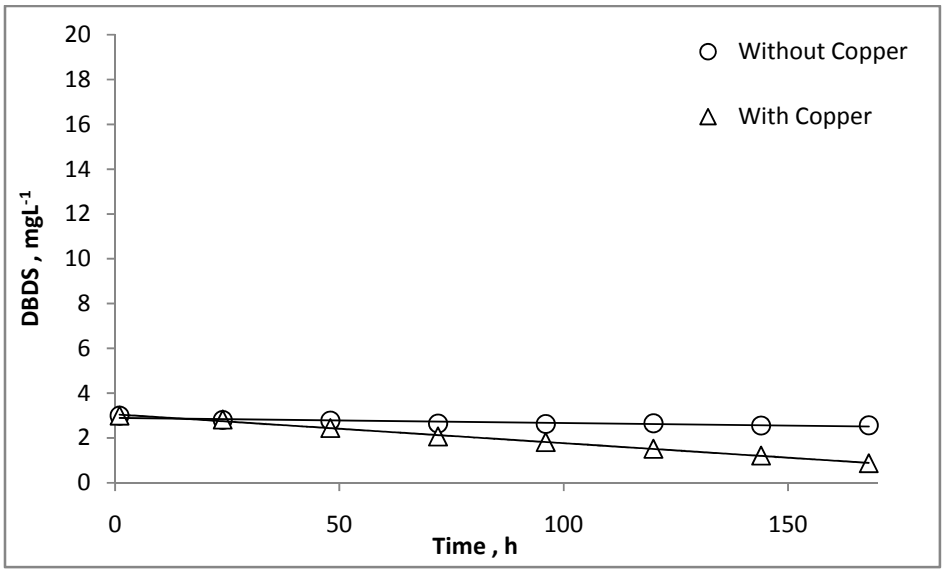


Fig 3.1. Depletion of 3 mgL^{-1} DBDS with time in the presence and in the absence of copper strips.

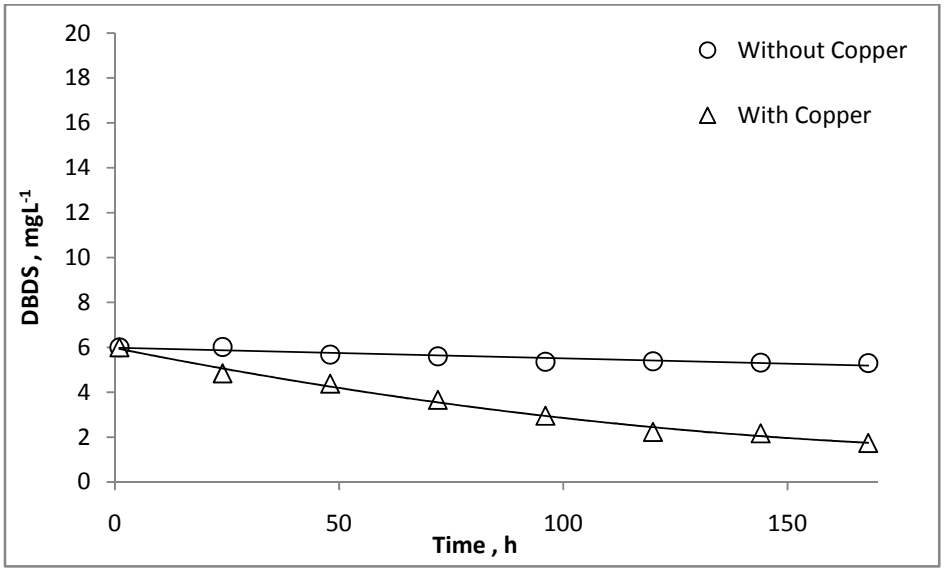


Fig 3.2. Depletion of 6 mgL^{-1} DBDS with time in the presence and in the absence of copper strips.

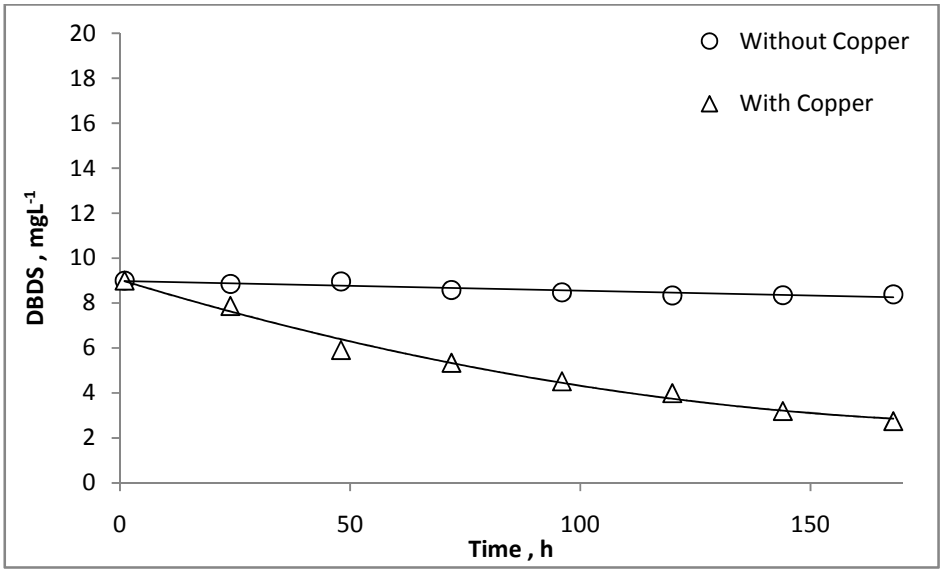


Fig 3.3. Depletion of 9 mgL^{-1} DBDS with time in the presence and in the absence of copper strips.

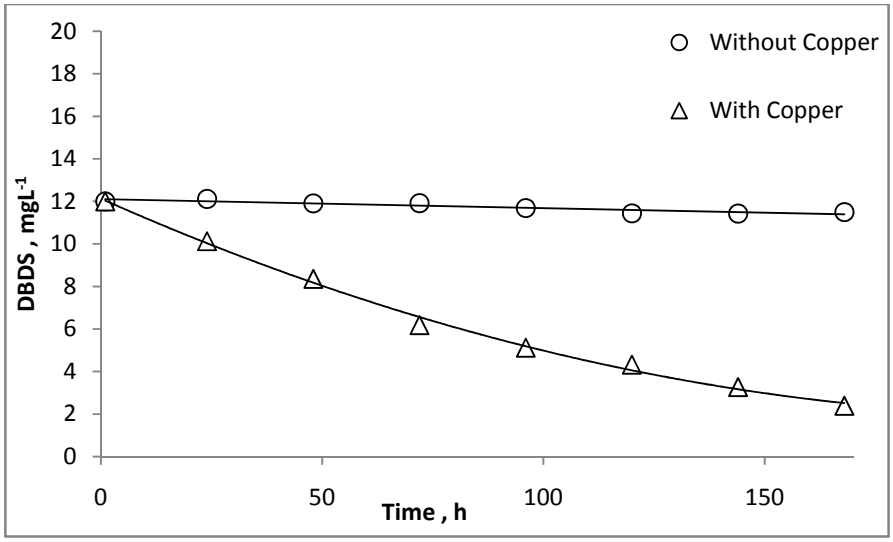


Fig 3.4. Depletion of 12 mgL^{-1} DBDS with time in the presence and in the absence of copper strips.

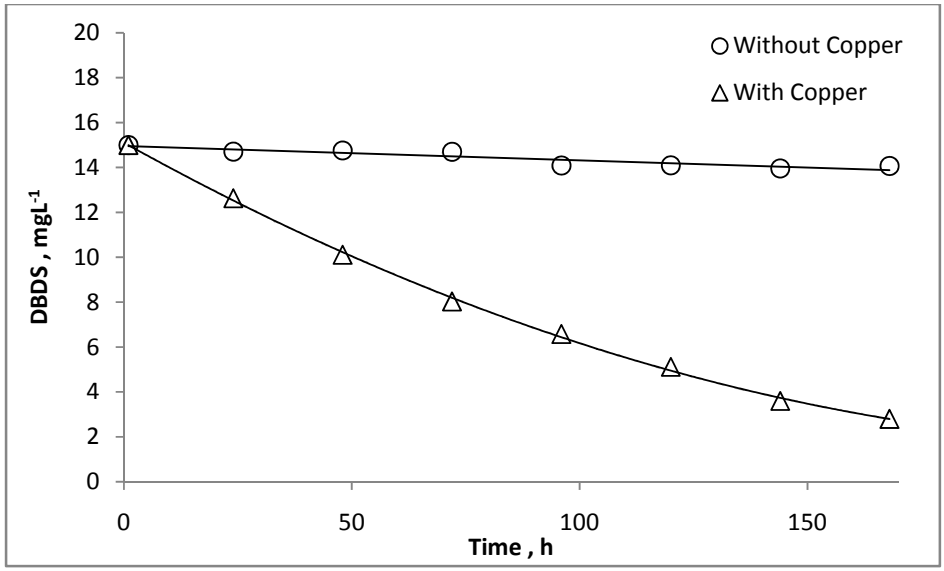


Fig 3.5. Depletion of 15 mgL^{-1} DBDS with time in the presence and in the absence of copper strips.

Table 3.1 The concentration of DBDS in mineral oil matrix kept at 150° C in contact with copper strips covered with insulating Kraft paper for different incubation times *t* in hours for different initial DBDS concentrations in mgL^{-1}

Initial DBDS concentration (mgL^{-1})	Final DBDS concentration in mgL^{-1} at time *t* (h)							
	1	24	48	72	96	120	144	168
3	3.00	2.83	2.45	2.07	1.82	1.52	1.22	0.88
6	6.00	4.84	4.38	3.66	2.95	2.23	2.17	1.74
9	9.00	7.87	5.91	5.34	4.52	3.99	3.20	2.75
12	12.00	10.13	8.36	6.18	5.12	4.32	3.27	2.39
15	15.00	12.63	10.11	8.03	6.58	5.12	3.60	2.80

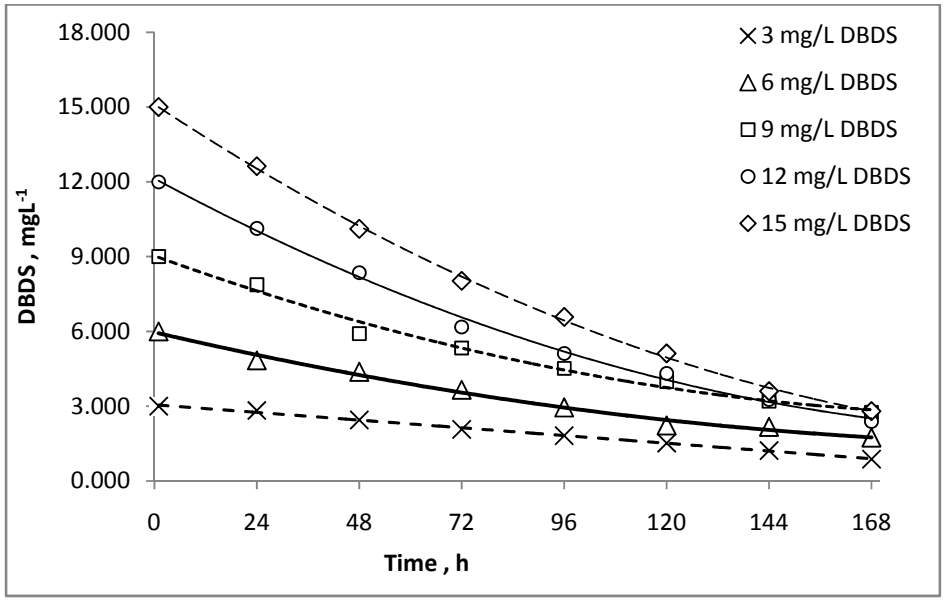


Fig 3.6. A plot of [A] versus t in hours for runs with different $[A]_o$ values; $[A]_o$ and [A] being the initial and final concentrations of DBDS in mineral oil at 150° C and kept in contact with copper strips covered with insulating Kraft paper.

Based on the assumption that the DBDS depletion is apparently a first order reaction, the observed reaction rate constant, *k*, was calculated from linear least squares plots of , $Ln([A]/[A]_o)$ versus incubation time *t* for each concentration which as is shown in Figs. 3.7 to 3.11. The observed k_{obs} values obtained for each concentration are given in Table 3.2.

Drawing the relationship between the observed reaction rate constant of DBDS depletion as a function of DBDS concentration is shown in Fig 3.12. The sudden increase in the observed reaction rate constant may refer to the onset of copper corrosion by the effect of DBDS. Thus, a concentration of 9 mgL^{-1} of DBDS could be considered as a threshold. However, below this concentration the corrosive effect of DBDS becomes negligible.

For the first time the DBDS corrosivity expressed as a threshold concentration was quantitatively determined. This conclusion would not be achieved without using the developed liquid-liquid extraction pretreatment step. This fact could not have been confirmed by the standard methods, IEC 62535 and ASTM D 1275 where all results concluded there were based on visual inspection of the copper strips after the incubation periods.

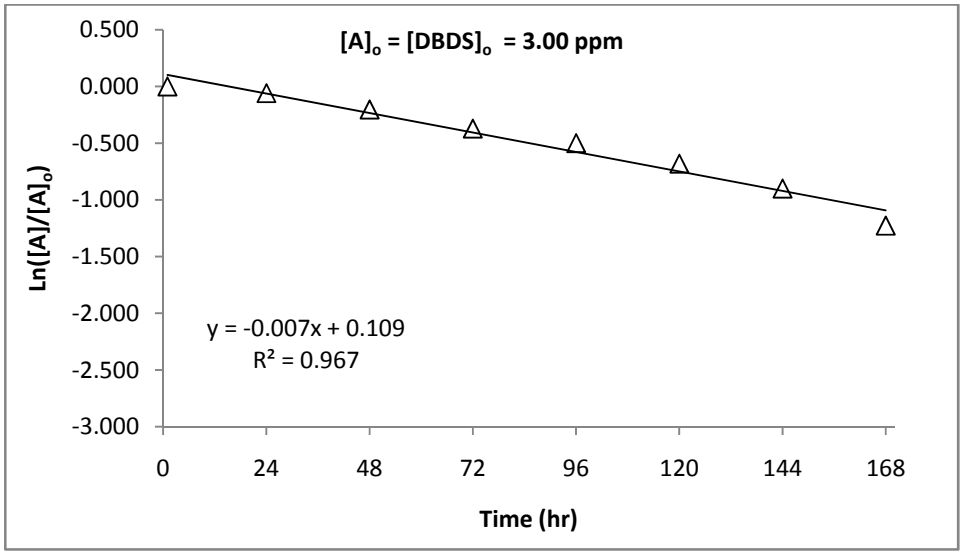


Fig 3.7. A plot of *Ln*([A]/[A]$_o$) versus incubation time where [A]$_o$ and [A] stand respectively for the initial and final concentrations of DBDS.

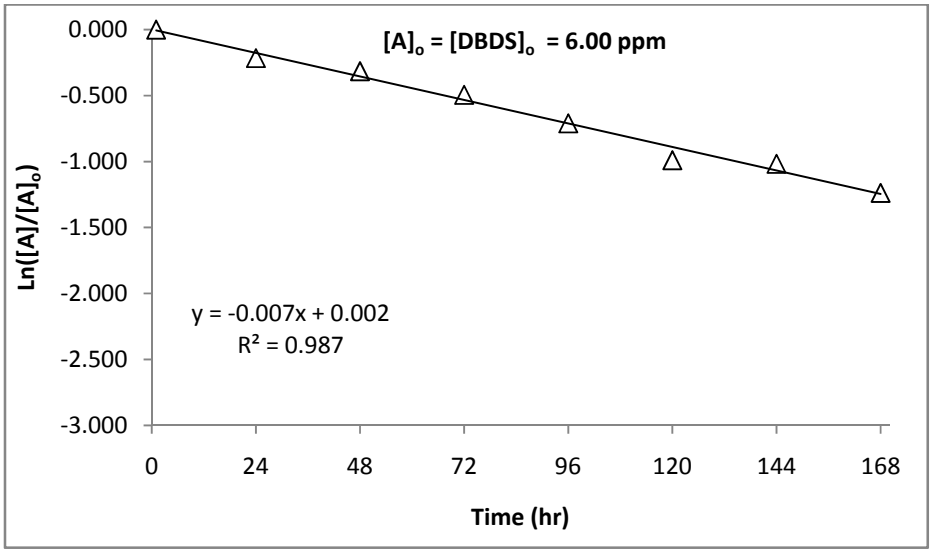


Fig 3.8. A plot of *Ln*([A]/[A]$_o$) versus incubation time where [A]$_o$ and [A] stand respectively for the initial and final concentrations of DBDS.

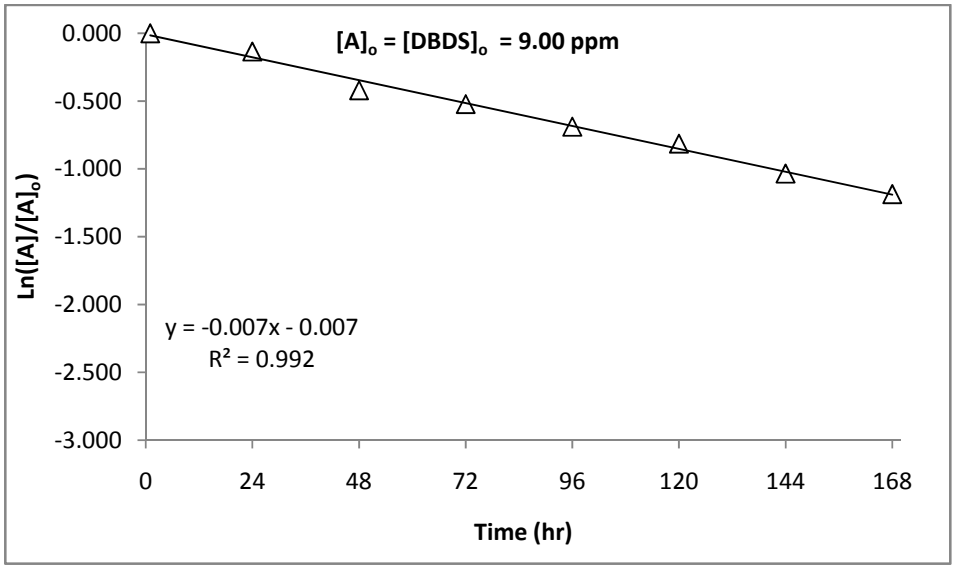


Fig 3.9. A plot of *Ln*([A]/[A]$_o$) versus incubation time where [A]$_o$ and [A] stand respectively for the initial and final concentrations of DBDS.

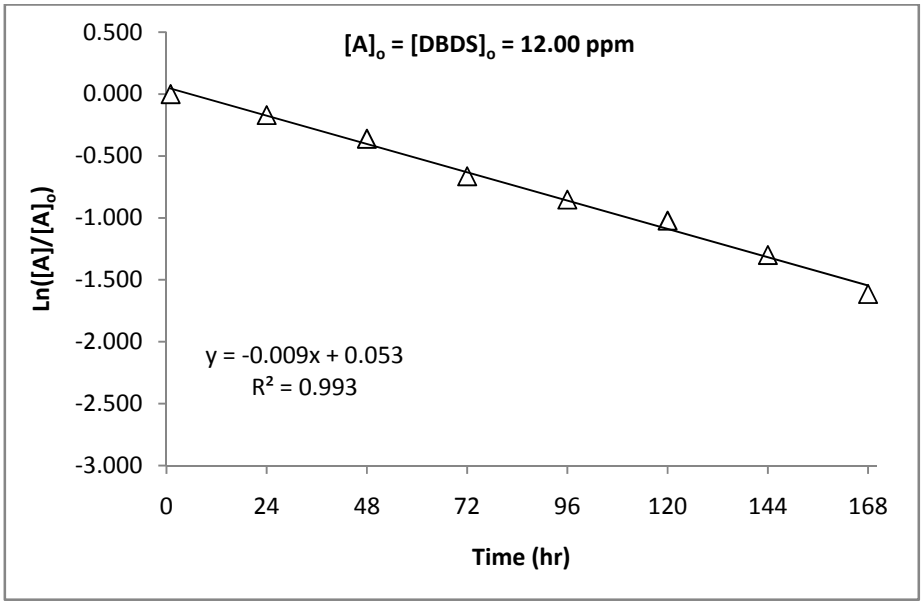


Fig 3.10. A plot of *Ln*([A]/[A]$_o$) versus incubation time where [A]$_o$ and [A] stand respectively for the initial and final concentrations of DBDS.

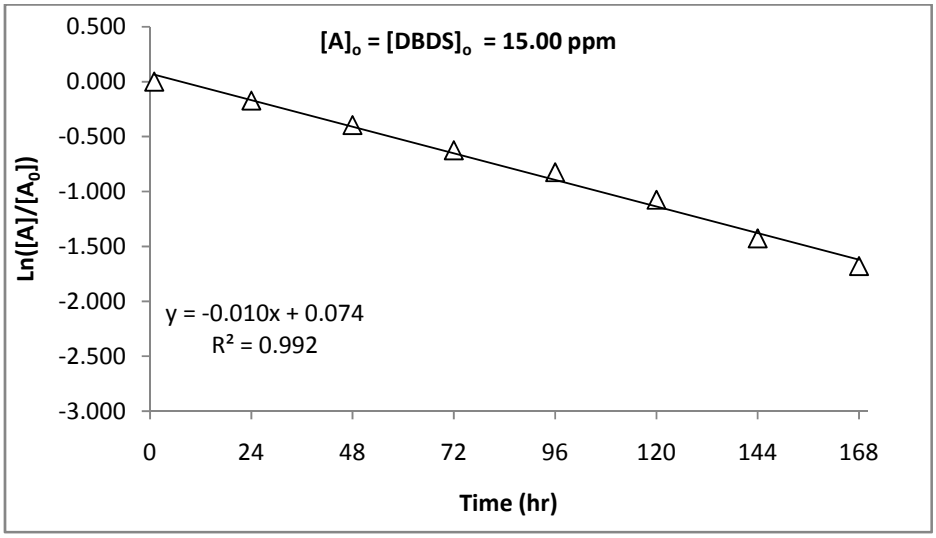


Fig 3.11. A plot of *Ln*([A]/[A]$_o$) versus incubation time where [A]$_o$ and [A] stand respectively for the initial and final concentrations of DBDS.

Table 3.2 Observed reaction rate constants, k_{obs}, corresponding to the initial DBDS concentrations

$[DBDS]_{initial}$ (mgL^{-1})	k_{obs} (h^{-1})
3	7.15×10^{-3}
6	7.42×10^{-3}
9	7.00×10^{-3}
12	9.40×10^{-3}
15	10.10×10^{-3}

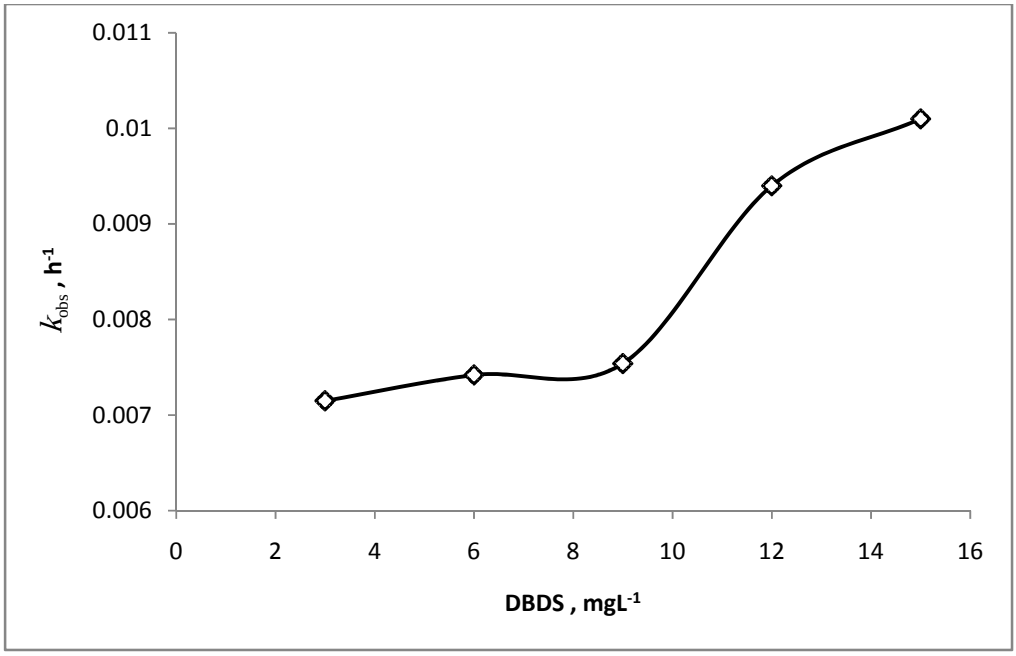


Fig 3.12. A plot of the observed depletion rate constants determined versus the initial DBDS concnetrations

Consequently the 9 mgL^{-1} threshold concentration of DBDS signifies an abrupt increase in this corrosive reaction. This result would not be confirmed using the IEC 62535 and ASTM D 1275 standard methods.

3.3.2 Effect of temperature on the copper corrosivity

To study the effect of temperature on the DBDS corrosivity for copper strips, the DBDS depletion was carried out for a solution of 150 mgL^{-1} DBDS at various incubation temperatures. The depletion rate constant was deduced at each temperature and these depletion rate constants were plotted versus the incubation temperature as given in Fig 3.13. This figure shows a break at a temperature of 100° C above which the DBDS depletion becomes significant. This confirms that the minimum effective temperature for DBDS to start its corrosive activities is 100° C.

When this experiment was conducted under the same conditions but the degree of corrosivity on copper strips was assessed visually according to standard methods, no sign of corrosion was clearly visualized on copper strips (Figs 3.14 - 3.18). One can conclude according to this kinetic study that copper sulfide may not start to form below a temperature of 100^{o} C even at longer periods of time.

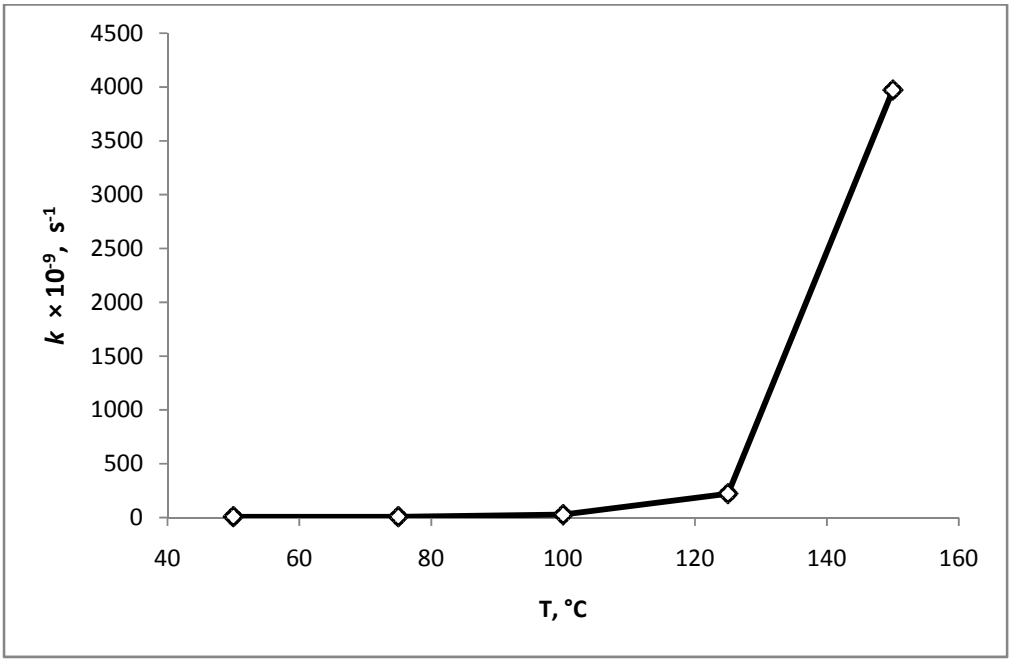


Fig 3.13. A plot of the depletion rate constants determined at various temperatures versus the corresponding temperatures

Temperature : 50° C	DBDS = 150 mgL^{-1}				
Time, h	24	48	72	96	120
IEC 62535					

Fig 3.14. Copper strips recovered after IEC-62535 examination for the depletion of 150 mgL^{-1} DBDS incubated at 50 °C.

Temperature : 75° C	DBDS = 150 mgL^{-1}				
Time, h	24	48	72	96	120
IEC 62535					

Fig 3.15. Copper strips recovered after IEC-62535 examination for the depletion of 150 mgL^{-1} DBDS incubated at 75 °C.

Temperature : 100° C	DBDS = 150 mgL^{-1}				
Time, h	24	48	72	96	120
IEC 62535					

Fig 3.16. Copper strips recovered after IEC-62535 examination for the depletion of 150 mgL^{-1} DBDS incubated at 100 °C .

Temperature : 125° C	DBDS = 150 mgL^{-1}				
Time, h	24	48	72	96	120
IEC 62535					

Fig 3.17 Copper strips recovered after IEC-62535 examination for the depletion of 150 mgL^{-1} DBDS incubated at 125 °C.

Temperature : 150° C	DBDS = 150 mgL^{-1}				
Time, h	24	48	72	96	120
IEC 62535					

Fig 3.18 Copper strips recovered after IEC-62535 examination for the depletion of 150 mgL^{-1} DBDS incubated at 150 °C.

3.4 Conclusion

The critical concentration of DBDS required to initiate its corrosive effect was determined quantitatively using acetonitrile liquid – liquid extraction followed by GC-ECD detection. Although a concentration of 9 mgL^{-1} which was determined by this work as a threshold concentration, the calculated reaction rates, *k*, showed that any concentration of DBDS in insulating oil can give rise to corrosion. This study shows that at operational temperatures below 100° C, copper conductors inside transformer units will not react to form copper sulfide even when the DBDS concentration in mineral oil matrix rises up to 150 mgL^{-1}.

Chapter Four

The minimum concentration of the passivator 1,2,3-Benzotriazol effective on the corrosivity of DBDS in mineral insulating oils

4.1 Introduction

One of the most effective solutions for quenching corrosive sulfur formation on copper conductors inside the power transformer units is the addition of metal passivator at mgL^{-1} levels. Passivators such as 1,2,3-Benzotriazol, BTA, or alkylated benzotriazole MBTA or Irgamet 39 (CIBA properties) are used in mineral insulating oils to block the active sites on the metal surface, hence, preventing the reaction between corrosive sulfur species and copper conductors inside the transformer unit. This passivation action is manifested by the formation of a molecular layer covering copper metal surfaces where the passivator reacts with copper and forms an organometallic film.

The metal passivator does not remove the corrosive compounds from the oil, however, it demonstrates some unexpected and undesired effects, such as the release of hydrogen and carbon oxides. This often leads to erroneous gas evolution test results [12]. Considering the quality of insulating oil, adding extra amount of metal passivator is not always of advantage.
Regarding BTA as a passivator, there was no record since 1970 about the stray gassing problems due to passivation in Japan [9]. 30 mgL^{-1} of 1,2,3-benzotriazol , BTA, and 100

mgL^{-1} of other alkylated BTA passivators are the recommended passivating levels in insulating oil.

Few reports are available about the minimum effective passivating level at which corrosive sulfur reaction can be retarded. Takashi et al [30] applied different passivator concentrations to mineral insulating oil samples spiked with 300 mgL^{-1} DBDS, 10 to 30 mgL^{-1} BTA and 100 mgL^{-1} Irgamet 39 were needed for this purpose. The total sulfur signal was obtained from copper sulfide deposited on copper strips using the wave length dispersive X-ray (WDX) system. It was quantitatively proved that corrosion by DBDS was controlled with the BTA passivator. The life time test of a passivator was determined [30] as follows: samples of 15 ml of mineral oil each and a copper strip were placed in six 20 ml vials in the open air and the vials were closed tightly with silicone caps. The six vials were heated for 8, 24, 48, 72, 96, and 168 h at 150 ◦C. The amount of sulfur formed on each of the copper strips was measured by WDX. When an amount of 10 mgL^{-1} of BTA was added to the oil, it was found that sulfur was not detected until after a period of 24 h. In the case of 30 mgL^{-1} of BTA, the corrosion control time has been extended to a period of 72 h. 30 mgL^{-1} of BTA was a little more effective in preventing corrosion than 100 mgL^{-1} of Irgamet 39. This may be attributed to the difference of adsorbability of the two species on the copper surface.

Augusta et al [36] proposed a study by which the minimum passivator concentration (below which the oil is corrosive) was determined in oil. In this study, several BTA derivative passivator "Irgamet 39" concentrations were investigated using IEC 62535 criterion after subjecting the passivator to an accelerated aging using IEC 61125 standard method.

Concentration range of 100 to 5 mgL^{-1} passivator was studied for this purpose. Table 4.1 indicates the corrosion results after incubation as per IEC 62535. It can also be noted that when the passivator concentrations are equal to or below a quantity of 21 mgL^{-1}, the test for potentially corrosive sulfur gives a positive result, thus, showing deposits of Cu_2S on copper and on the insulating paper. Concentrations between 51 mgL^{-1} (negative result) and 21 mgL^{-1} (positive result) have not yet been tested. This study concluded that the minimum concentration of the BTA derivative passivator is considered to be 50 mgL^{-1}.

Amimoto et al [16] confirmed the passivator-copper system by testing the complex layers by time-of-flight secondary ion mass spectrometer (TOF-SIMS) which showed that several peaks originating from the passivator-copper system were observed in the spectrum.

The minimum concentration of the passivators, BTA and its derivatives, was estimated qualitatively [16, 30, 36] using the standard methods, IEC 62535 or ASTM D 1275. The purpose of the work here is to determine quantitatively the minimum BTA concentration below which corrosive sulfur compounds such as DBDS if present in the mineral insulating oil would be effective. BTA will be determined quantitatively using the liquid – liquid extraction pretreatment step followed by/ HPLC/UV method as designed in Chapter 2.

Table 4.1. Results of the IEC-62535 test for potentially corrosive sulfur done after oil aging [36].

Irgamet 39 (mgL^{-1})	Copper	Paper	Final Result		
-	-	-	Control	 Paper	
100	Negative	Negative	Negative	 Copper	 Paper
82	Negative	Negative	Negative	 Copper	 Paper
74	Negative	Negative	Negative	 Copper	 Paper
51	Negative	Negative	Negative	 Copper	 Paper
21	Positive	Positive	Positive	 Copper	 Paper
<5	Positive	Positive	Positive	 Copper	 Paper

4.2 Experimental and methods

Four groups of mineral insulating oil sample solutions were prepared in which each group is comprised of six mineral oil sample solutions containing concentration of 10, 50, 150 or 300 mgL^{-1} DBDS and varied BTA concentrations from 0 to 70 mgL^{-1}. All sample solutions were incubated at room temperature and at a temperature of 150° C for 72 h according to the IEC 62535 standard method. All oil sample solutions were purged with argon to minimize the contact with the atmospheric air. After the incubation period, the concentrations of DBDS and BTA were determined according to the liquid– liquid extraction pretreatment followed by GC-ECD/HPLC detection. Alternatively, another 9 groups of mineral insulating oil sample solutions were prepared in which each group is comprised of four mineral oil sample solutions containing fixed concentrations of 0, 2, 3, 4, 5, 10, 30 50 and 70 mgL^{-1} of BTA and varied concentrations of 10 to 300 mgL^{-1} of DBDS. All sample solutions were treated in the same manner as the first group of oil samples mentioned above.

4.3 Results and discussion

Limited studies were made to determine the minimum concentration of BTA and its derivatives above which DBDS starts the corrosion cycle within the mineral oil matrix. The BTA derivative passivator minimum concentration was estimated as 50 mgL^{-1} [36]. Toyama et al [20] reported a minimum concentration of 30 mgL^{-1} of 1,2,3-Benzotriazol.

The DBDS corrosivity and the depletion of BTA as a corrosion inhibitor in the insulating oil under heat conditions in the presence and absence of copper strips were studied using two analytical protocols as mentioned in the experimental section. In the first protocol, the

depletion of BTA concentration was investigated in the presence of various DBDS concentrations under different conditions. Figs. 4.1-4.4 indicate that DBDS does not show any corrosivity in the insulating oil at the room temperature and in the absence of copper, irrespective of its concentration that was ranged from 10 to 300 mgL^{-1}. The slope of the calibration curve for BTA was almost the same in the presence of 10, 50, 150 and 300 mgL^{-1} DBDS, thus, no measurable BTA depletion was detected as a result of its action against the DBDS corrosion activity in the oil. However, as manifested by the BTA depletion profile (Figs. 4.1-4.4), DBDS acted as a source of corrosion in the oil when the incubation temperature of the oil samples was raised to 150^{o}C. The corrosion was more significant in the presence of copper strips and at a temperature of 150^{o}C . Figs. 4.1-4.4 show that the depletion profile of BTA under any condition is almost the same irrespective of the DBDS concentration.

On the other hand, the second protocol was conducted to study the depletion of DBDS in the presence of fixed concentrations of BTA in order to determine the minimum BTA concentration that quenches the DBDS corrosion activity. Thus, as mentioned earlier, various groups of insulating oil samples each containing varied concentrations of DBDS (10-300 mgL^{-1} DBDS) and a fixed concentration of BTA were prepared. Each group has been incubated under various conditions, namely, room temperature, 150^{o}C in the absence and in the presence of copper strip. All samples were tested for their DBDS concentration using GC-ECD after the liquid-liquid extraction pretreatment step mentioned earlier.

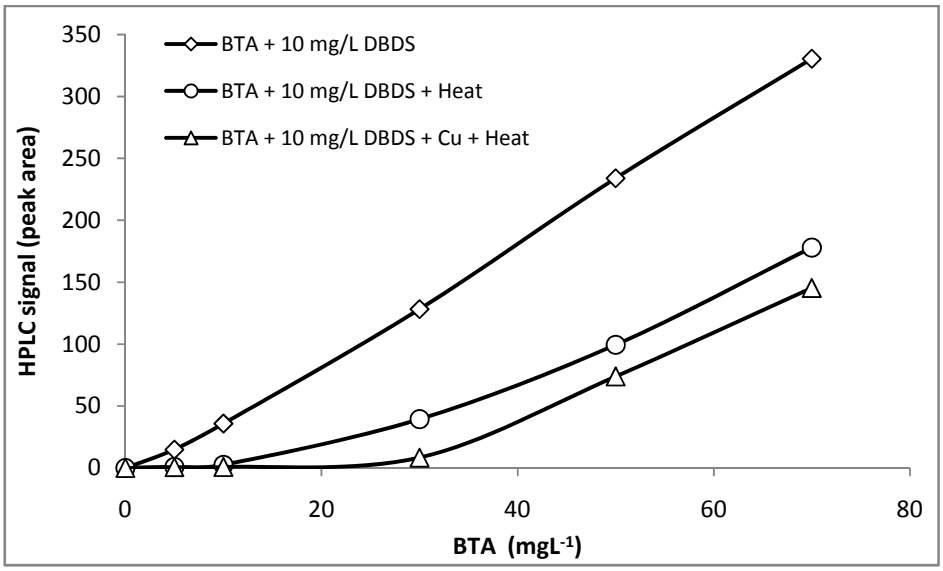


Fig 4.1 HPLC signal exprssed as peak areas recorded for various mineral oil sample solutions comprising different BTA concentrations and a fixed (10 mgL^{-1} DBDS) DBDS concentration after the liquid-liquid extraction pretreatment step in the presence and in the absence of copper strips with and without heating.

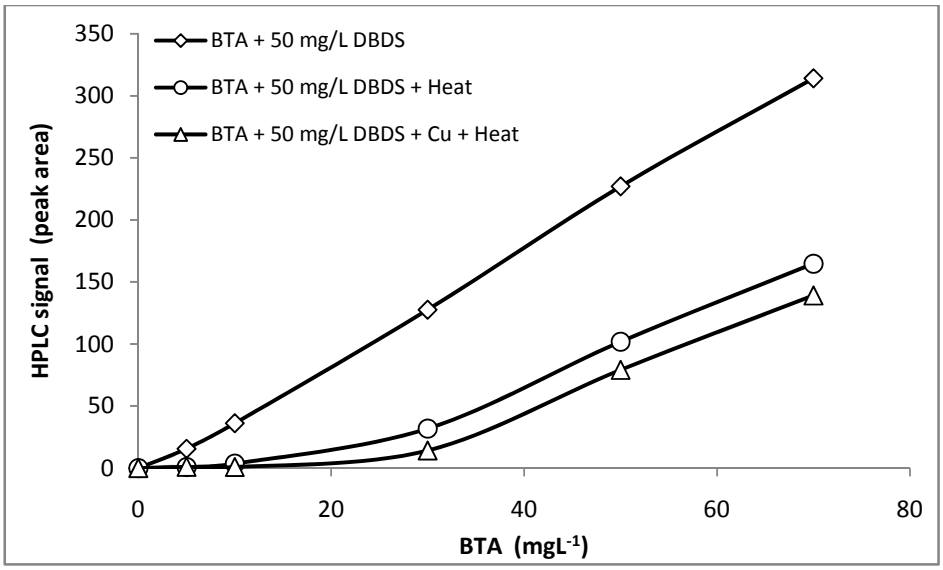


Fig 4.2 HPLC signal exprssed as peak areas recorded for various mineral oil sample solutions comprising different BTA concentrations and a fixed (50 mgL^{-1} DBDS) DBDS concentration after the liquid-liquid extraction pretreatment step in the presence and in the absence of copper strips with and without heating.

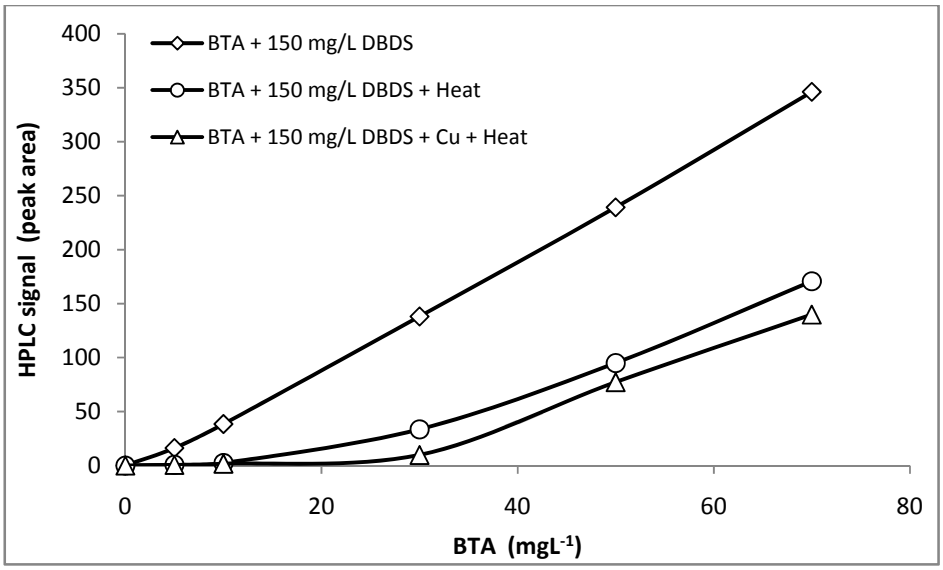


Fig 4.3 HPLC signal exprssed as peak areas recorded for various mineral oil sample solutions comprising different BTA concentrations and a fixed (150 mgL^{-1} DBDS) DBDS concentration after the liquid-liquid extraction pretreatment step in the presence and in the absence of copper strips with and without heating.

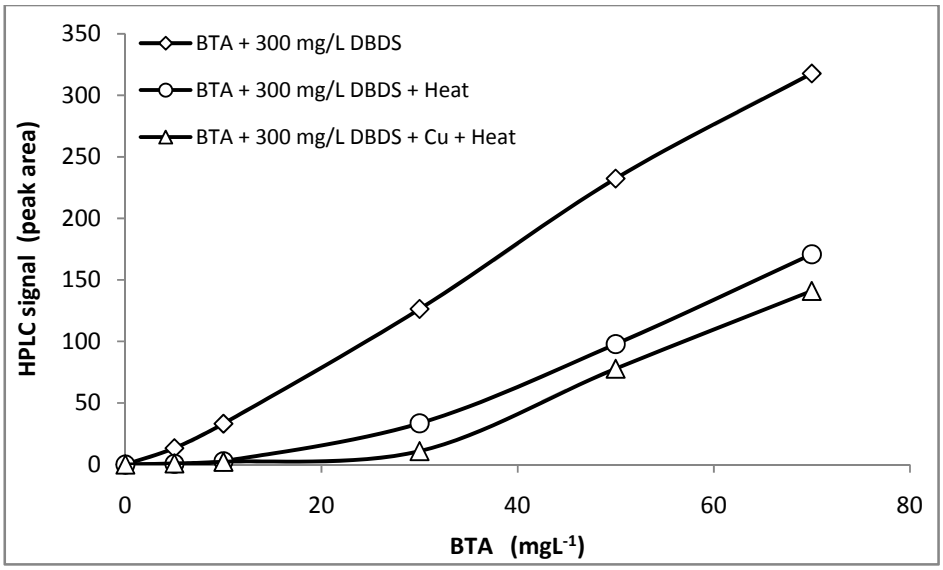


Fig 4.4 HPLC signal exprssed as peak areas recorded for various mineral oil sample solutions comprising different BTA concentrations and a fixed (300 mgL^{-1} DBDS) DBDS concentration after the liquid-liquid extraction pretreatment step in the presence and in the absence of copper strips with and without heating.

Figs. 4.5-4.13 show the DBDS depletion profile in presence of various BTA concentrations, namely, 0 BTA (Fig. 4.5), 2 BTA (Fig. 4.6), , 3 BTA (Fig. 4.7), 4 BTA (Fig. 4.8), , 5 BTA (Fig. 4.9), 10 BTA (Fig. 4.10), 30 BTA (Fig. 4.11), 50 BTA (Fig. 4.12), 70 BTA (Fig. 4.13). All the calibration curves for DBDS concentrations in all oil samples against the GC-ECD signals have almost the same slopes when incubated at room temperature or at a temperature of 150° C, but in the absence of copper strips. Thus, there was no significant depletion for DBDS in the oil under these conditions that is, DBDS had no any corrosive activity under these conditions. However, when copper strips were inserted in the oil samples and incubated at 150° C, the calibration curve showed a significant DBDS depletion in the absence of BTA passivator (Fig. 4.5), and the extent of the depletion has decreased with the concentration of BTA (Figs. 4.6-4.8) until it has disappeared when the BTA concentration becomes $\geq$5 mgL^{-1} DBDS (Fig. 4.9-4.13). Consequently, the minimum BTA concentration that is necessary to quench the effect of DBDS is 5 mgL^{-1} and any increase in this concentration would not make any difference.

The above quantitative conclusion regarding the minimum concentration of BTA by which DBDS effect can be suppressed is in a good agreement with the conventional IEC-62535 criterion. Figs 4.14 to 4.17 illustrate the visual corrosion for the four oil groups having different DBDS concentrations. A quantity of 5 mgL^{-1} BTA was found to be enough to eliminate the corrosion behavior of DBDS at any concentration levels.

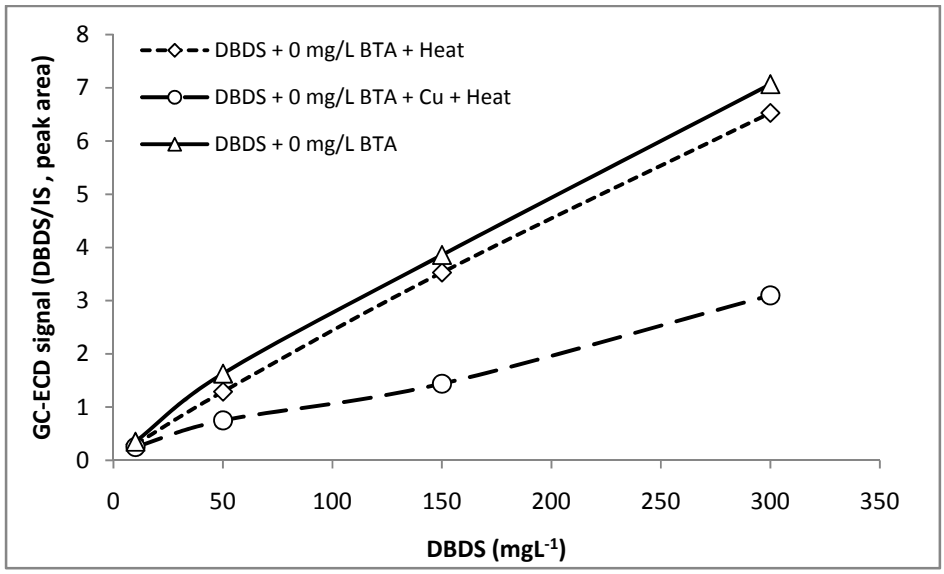


Fig 4.5 GC-ECD signal exprssed as peak areas recorded for various mineral oil sample solutions comprising different DBDS concentrations and a fixed (0 mgL^{-1} BTA) BTA concentration after the liquid-liquid extraction pretreatment step in the presence and in the absence of copper strips with and without heating.

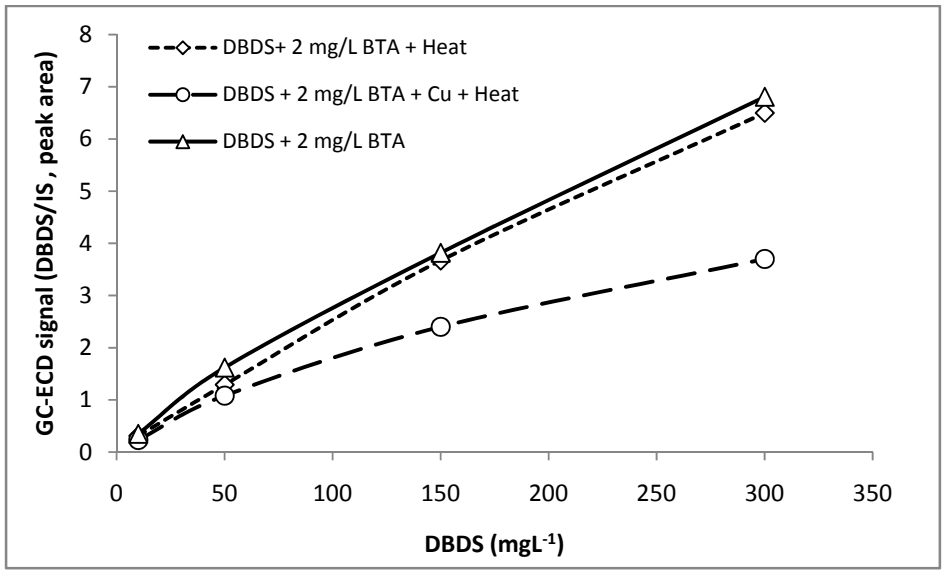


Fig 4.6 GC-ECD signal exprssed as peak areas recorded for various mineral oil sample solutions comprising different DBDS concentrations and a fixed (2 mgL^{-1} BTA) BTA concentration after the liquid-liquid extraction pretreatment step in the presence and in the absence of copper strips with and without heating.

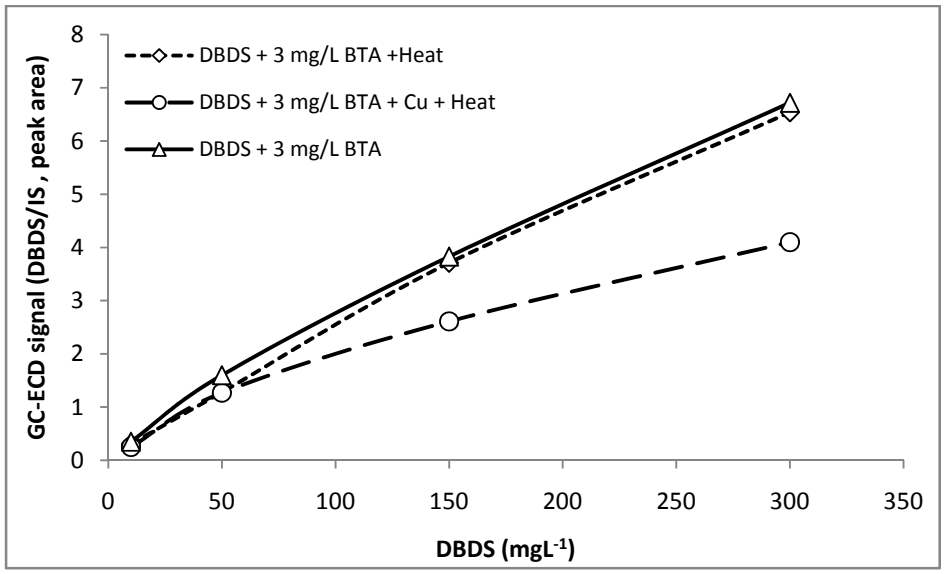


Fig 4.7 GC-ECD signal exprssed as peak areas recorded for various mineral oil sample solutions comprising different DBDS concentrations and a fixed (3 mgL^{-1} BTA) BTA concentration after the liquid-liquid extraction pretreatment step in the presence and in the absence of copper strips with and without heating.

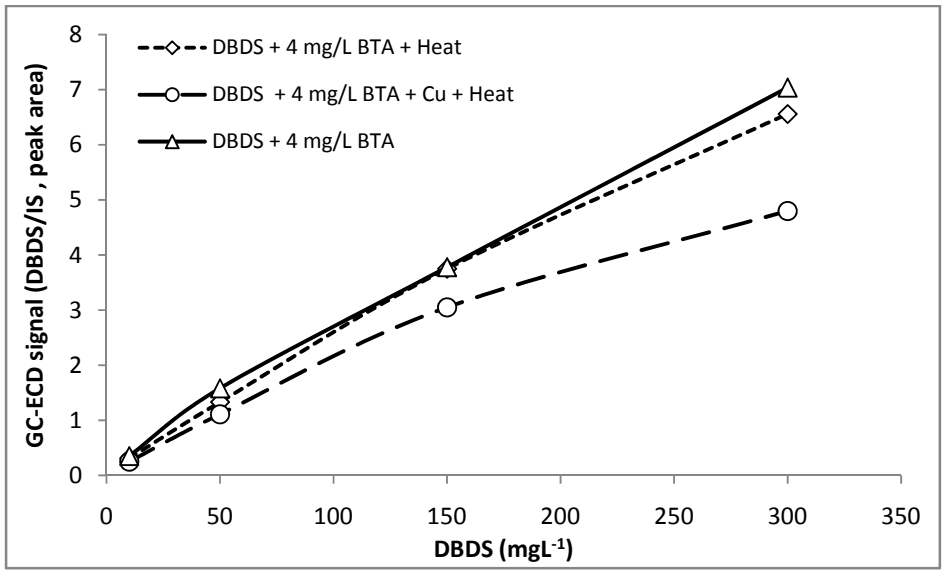


Fig 4.8 GC-ECD signal exprssed as peak areas recorded for various mineral oil sample solutions comprising different DBDS concentrations and a fixed (4 mgL^{-1} BTA) BTA concentration after the liquid-liquid extraction pretreatment step in the presence and in the absence of copper strips with and without heating.

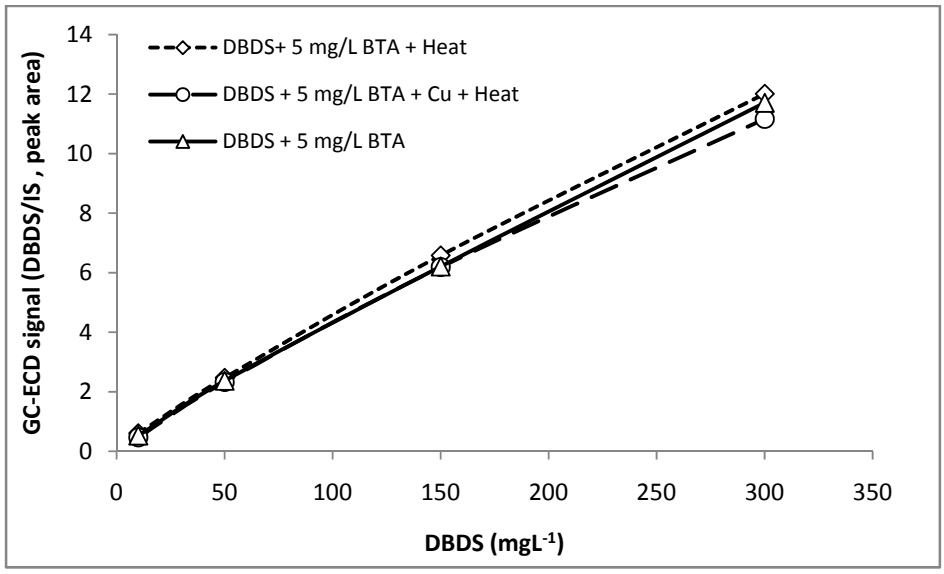


Fig 4.9 GC-ECD signal exprssed as peak areas recorded for various mineral oil sample solutions comprising different DBDS concentrations and a fixed (5 mgL^{-1} BTA) BTA concentration after the liquid-liquid extraction pretreatment step in the presence and in the absence of copper strips with and without heating.

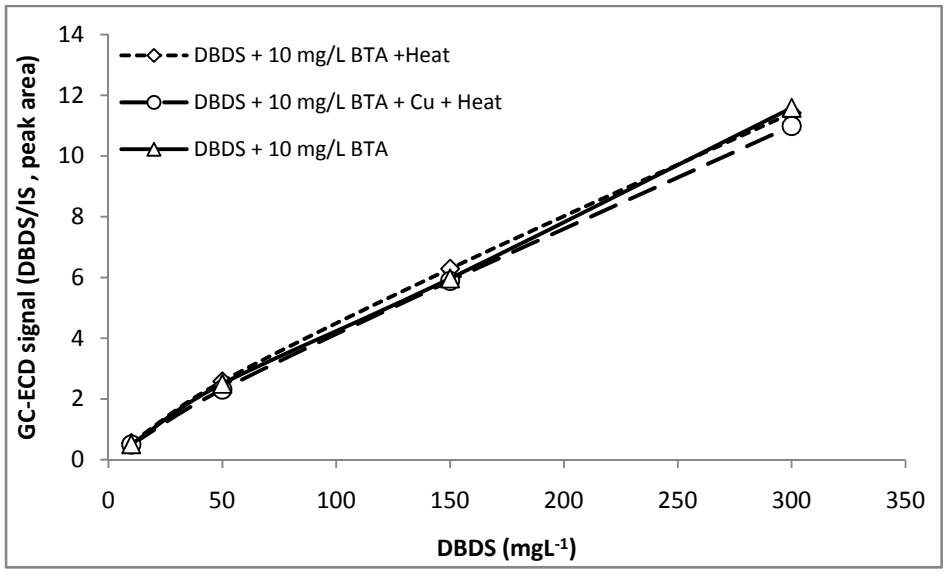


Fig 4.10 GC-ECD signal exprssed as peak areas recorded for various mineral oil sample solutions comprising different DBDS concentrations and a fixed (10 mgL^{-1} BTA) BTA concentration after the liquid-liquid extraction pretreatment step in the presence and in the absence of copper strips with and without heating.

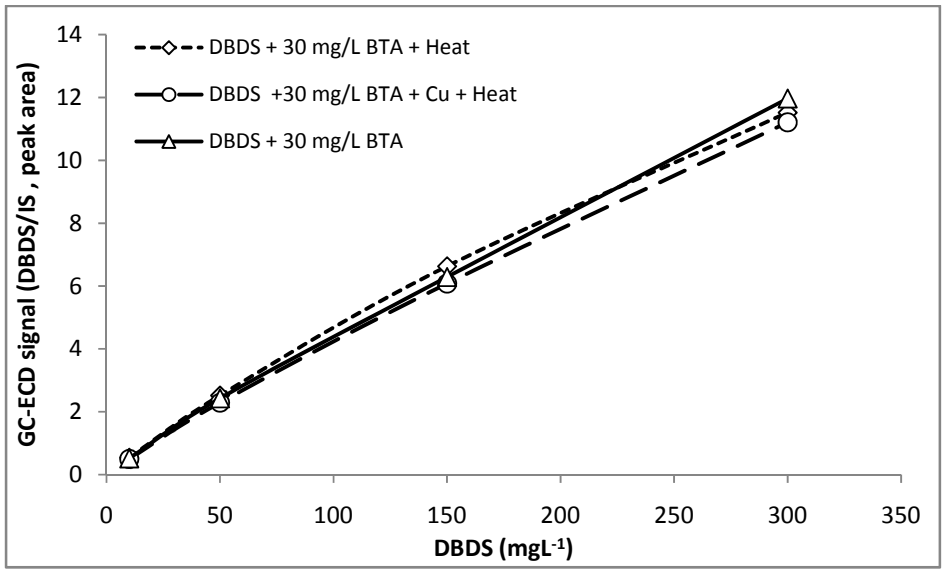


Fig 4.11 GC-ECD signal exprssed as peak areas recorded for various mineral oil sample solutions comprising different DBDS concentrations and a fixed (30 mgL^{-1} BTA) BTA concentration after the liquid-liquid extraction pretreatment step in the presence and in the absence of copper strips with and without heating.

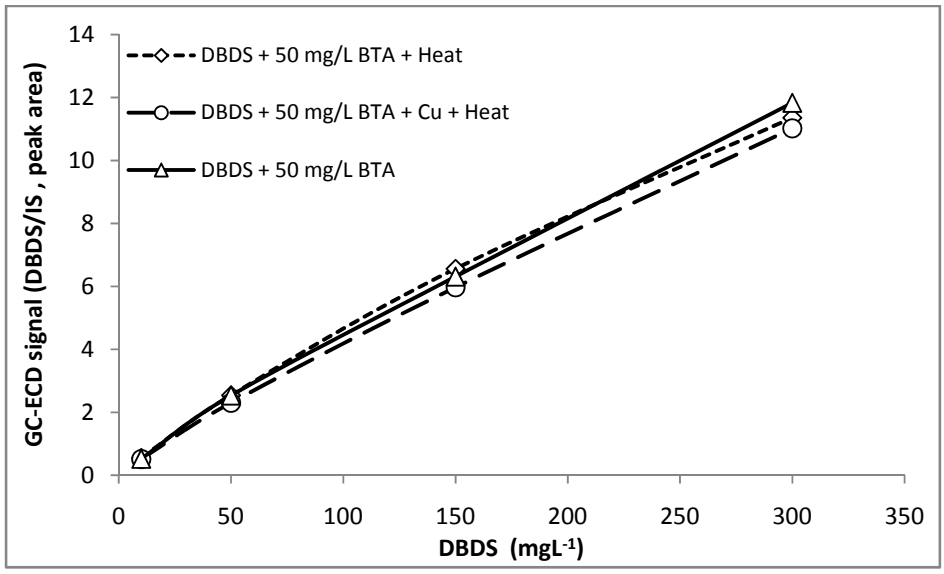


Fig 4.12 GC-ECD signal exprssed as peak areas recorded for various mineral oil sample solutions comprising different DBDS concentrations and a fixed (50 mgL^{-1} BTA) BTA concentration after the liquid-liquid extraction pretreatment step in the presence and in the absence of copper strips with and without heating.

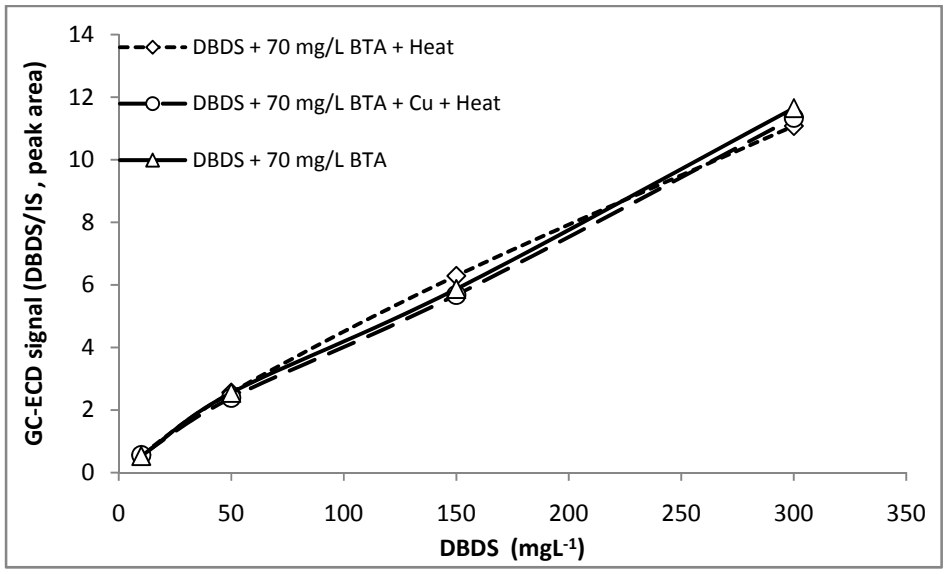


Fig 4.13 GC-ECD signal exprssed as peak areas recorded for various mineral oil sample solutions comprising different DBDS concentrations and a fixed (70 mgL^{-1} BTA) BTA concentration after the liquid-liquid extraction pretreatment step in the presence and in the absence of copper strips with and without heating.

DBDS = 10 mgL^{-1}					
BTA, mgL^{-1}	0	2	3	4	5
IEC-62535					

DBDS = 50 mgL^{-1}					
BTA, mgL^{-1}	0	2	3	4	5
IEC-62535					

Fig 4.14. copper strips recovered after IEC-62535 examination for two different oil groups having 10 and 50 mgL^{-1} DBDS and various BTA concentrations .

DBDS = 150 mgL^{-1}					
BTA, mgL^{-1}	0	2	3	4	5
IEC-62535					

DBDS = 300 mgL^{-1}					
BTA, mgL^{-1}	0	2	3	4	5
IEC-62535					

Fig 4.15. copper strips recovered after IEC-62535 examination for two different oil groups having 150 and 300 mgL^{-1} DBDS and various BTA concentrations.

DBDS = 10 mgL^{-1}						
BTA, mgL^{-1}	0	5	10	30	50	70
IEC-62535						

DBDS = 50 mgL^{-1}						
BTA, mgL^{-1}	0	5	10	30	50	70
IEC-62535						

Fig 4.16. copper strips recovered after IEC-62535 examination for two different oil groups having 10 and 50 mgL^{-1} DBDS and various BTA concentrations.

DBDS = 150 mgL^{-1}						
BTA, mgL^{-1}	0	5	10	30	50	70
IEC-62535						

DBDS = 300 mgL^{-1}						
BTA, mgL^{-1}	0	5	10	30	50	70
IEC-62535						

Fig 4.17. copper strips recovered after IEC-62535 examination for two different oil groups having 150 and 300 mgL^{-1} DBDS and various BTA concentrations.

4.4 Conclusion

The current work quantitatively determined that an amount of 5 mgL^{-1} BTA is the minimum concentration required to retard the formation of copper sulfide when DBDS is present in insulating oil matrix. This may reduce the side effects of benzotriazole passivators by releasing dissolved gases in the oil which is considered to be a source of confusion. Furthermore, in this study a subtractive assay technique was applied to estimate the effective concentration of 5 mgL^{-1} benzotriazole in passivator-copper system which is the minimum benzotriazole concentration itself, 5 mgL^{-1}.

Chapter 5

Assessment of some antioxidant additives as oxidation inhibitors in mineral oil and their resistance to oxidation

5.1 Introduction

Antioxidant additives in mineral oils are mandatory to reduce the formation of oxidation by-products due to oil aging effects such as high operational temperatures, high water content, dissolved oxygen and other factors [5]. The oxidation by-products were extensively investigated and it was proven that the formation of compounds like acids, ketones, peroxides, alcohols, aldehydes affect the insulating function of the oil [4, 42]. As a result, the cooling efficiency inside the power transformer unit will decrease leading to electrical failures. To reduce the formation of those undesirable oxidation by-products, the oxidation stability of the insulating oil has to be improved. This elongates the lifetime of the oil and consequently the power transformer unit efficiency will be improved.

Certain additives like antioxidants and metal deactivators, will help in increasing the oxidation stability of the oil. These additives neutralize the peroxy radicals responsible for the formation of polar oxidation by-products and minimize acid formation [32]. However, monitoring the concentration levels of such additives is considered an important demand as they continue to be effective in the oil until their concentration is significantly depleted. As a result of the uncontrolled depletion in the concentrations of the additive, the oil becomes

reactive and the formation of oxidation by-products will take place again. The need for monitoring the presence of these polar oxidation compounds in the oil matrix requires efficient analytical methods that signal the real dangerous level of such compounds and their effect on the oil quality. Several methods are available to determine the presence of the oxidation by-products in insulating oil. ASTM 3487 [7] includes the most important chemical, physical and electrical tests to be conducted to determine the levels of the oxidation compounds in mineral insulating oil. These tests include: dielectric break down, neutralization number, interfacial tension, dielectric dissipation factor, specific gravity, resistivity, etc. Some of these tests may be insensitive to impurities and do not give a direct conclusion about the real presence of polar oxidation compounds in the oil, while others like interfacial tension and neutralization number are highly sensitive and may produce a rejection value [43]. However, the above mentioned analytical parameters cannot give a direct statement about the oxidation stability profile.

ASTM D 2440 [44] or IEC 61125 [45] are standard methods applied to provide stress conditions on the mineral oil samples in order to stimulate the oxidation process. The resulting oxidation products can be assessed quantitatively by the neutralization number or interfacial tension according to the standard methods, ASTM D 974 [46] and ASTM D 971 [47], respectively. As a result of the stress conditions as per the ASTM D 2440 method where oxygen stream and heating are applied on the oil sample, oxidation by-products will be formed depending on the degree of the oil stability. The neutralization number (ASTM D 974) measures the acid content resulting from the oxidation process. The higher the acidity and the sludge content the lower the oxidation resistance of the oil. Interfacial tension (IFT)

is a sensitive physical parameter for the presence of oxidation polar compounds in the oil. The lower the IFT the higher the content of these polar compounds in the oil and thus, the lower the oxidation stability

Percherancier et al [43] used FTIR technique to detect additives like DBPC and BTA in insulating oil by measuring the intensity of the characteristic functional group band for each additive. Other contaminations such as oxidation by-products in the oil were also detected by the same technique. ASTM D 2668-07 standard test method [33] has been developed for the determination of DBPC and DBP by measuring their absorbance in the oil sample using FTIR technique. Neto et al [4] used FTIR to study quantitatively and indirectly the effect of a group of antioxidants (phenolic, cresol antioxidants) on the oxidation stability of insulating mineral oil. Based on Neto and coworkers, mineral oil samples were artificially oxidized using ASTM D 2440 and then the oxidation stability for the oil samples were assessed by measuring the level of degradation indicated by the carbonyl band. The area under the carbonyl band (around 1713 cm^{-1}) in the FTIR spectrum can be monitored and compared to that obtained for the new none oxidized oil.

Krishnamoorthy et al [42] estimated qualitatively the oxidation stability performance for insulating oil samples by comparing two antioxidants, DBPC and BTA using ASTM D 2272 [48]. Even at lower concentrations, it was concluded that BTA is more effective antioxidant compared to DBPC. Wiklund et al [23] showed quantitatively that the concentrations of BTA and its derivatives were subjected to a sever decay/oxidation during artificial thermal aging process (according to IEC-62535 criteria). It was found that the rapid depletion of

BTA concentration is independent of the oxidation by-products such as aldehydes, ketones, esters or carboxylic acids. Hydroperoxides in insulating oil matrix were determined to be the responsible for the BTA depletion.

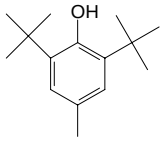
In this work, some antioxidants were assessed as oxidation inhibitors in mineral insulating oil by measuring the neutralization number and the interfacial tension of mixtures of oil samples and certain quantities of each of these additives and their performance was evaluated according to the standard methods, ASTM974 and ASTM 971 D, respectively. The oxidation stability of the antioxidant additives was evaluated by using the liquid-liquid extraction pretreatment followed by GC/HPLC. The degree of oxidation stability of each additive was found to be proportional to the quantity depleted from the additive after an incubation period of oil samples containing these additives under the above mentioned stress conditions.

5.2 Experimental and methods

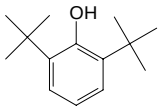
The oxidation stability of some mineral insulating oil antioxidants was investigated. The antioxidants studied included: 2,6-di-*tert*-butyl-*p*-cresol (DBPC), 2,6-di-*tert*-butyl-phenol (DBP), dibenzyl disulfide (DBDS), 2-*tert*-butyl-*p*-cresol (2-tBPC), alkylation-α-naphthylamine, BTA and methylated-BTA. The concentration of each of these antioxidants was added to the mineral insulating oil samples based on the values suggested to simulate the actual condition in the oil matrix [13, 15, 16, 17, 18, 36, 49, 50]. A concentration of 0.30% w/v of each of the antioxidants in mineral oil was prepared. The concentration of

DBDS was 150 mgL^{-1} and that of BTA and methylated BTA was 30 mgL^{-1} according to the recommended concentration levels of such compounds in the oil.

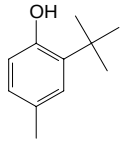
Each oil sample containing a specific antioxidant was subjected to an artificial thermal aging as per the ASTM D 2440 standard method for several time intervals (24, 48, 72, 96 and 120 h).



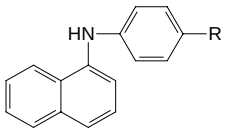
2,6-di-*tert*-butyl-*p*-cresol (DBPC)



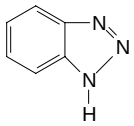
2,6-di-*tert*-butyl-phenol (DBP)



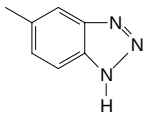
2-*tert*-butyl-*p*-cresol (2-tBPC)



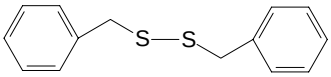
Alkylation-α-naphthylamine



BTA



Methylated -BTA



Dibenzyl disulfide (DBDS)

After each thermal aging interval, oil samples were removed and tested for their neutralization number and interfacial tension according to the ASTM 974 D and ASTM 970 D. Furthermore, another set of oil samples were pretreated by liquid-liquid extraction followed by quantitative determination using GC/HPLC techniques. The experimental setup

(Fig 5.1) used in this study for the incubation of oil samples under stress conditions was the same as that used by Neto et al [4].

5.3 Results and discussions

5.3.1 Assessment of mineral oil stability in the presence of various antioxidants using the conventional standard methods

Mineral oil samples were subjected to artificial accelerated aging at a temperature of about 100° C with a continuous oxygen flow of 1.0L/h in presence of a metallic catalyst. The time periods of the tests were as follows: 24, 48, 72, 96 and 120 h. The neutralization number and interfacial tension of the resulting oxidation by-products were determined.

Fig 5.2 shows the results obtained for neutralization numbers after subjecting insulating oil samples containing seven different antioxidants to standard accelerated aging conditions. Neutralization number represents the acid content generated from the mineral oil oxidation. Excluding the case where copper strip is added to the oil sample that contains DBDS antioxidant, the highest acidity was observed for the oil solutions containing methylated BTA and 2-*tert*-butyl-*p*-cresol. BTA showed relatively high neutralization numbers compared to the remaining antioxidants.

An oil sample solution containing DBDS without copper strip and in presence of alkylation-α-naphthylamine, DBP or DBPC showed relatively low neutralization numbers indicating a relatively high efficiency as antioxidants. Three of these antioxidants were phenolic with steric hindered discrepancy.

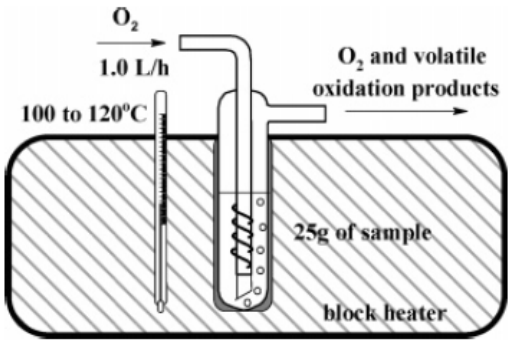


Fig 5.1. The experimental setup for the accelerated aging study as per ASTM D2440 [4].

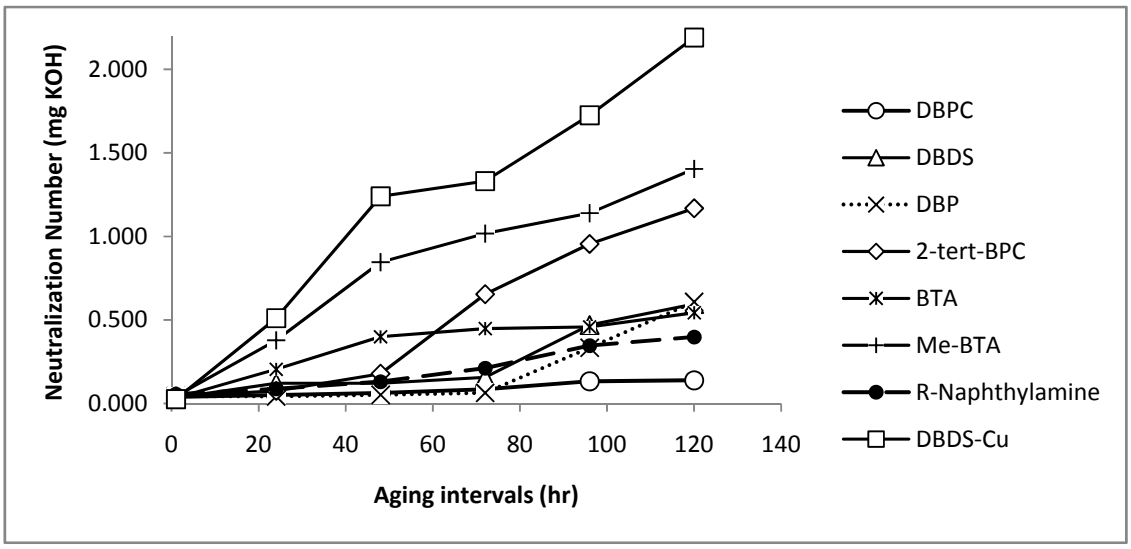


Fig 5.2. Neutralization number after accelerated aging for several oil samples containing different antioxidants. DBDS-Cu refers to the case where a copper strip was added into the oil sample solution with DBDS.

DBPC showed the lowest neutralization number and thus the relatively highest oil oxidation inhibition. This may be ascribed to the fact that DBPC is the most strictly hindered antioxidant [4, 5]. When copper strip was added to the oil-DBDS sample solution, the relatively highest acid number was observed (Fig. 5.2) indicating that DBDS is losing its ability as an antioxidant and started to act as a corrosive sulfur component.

The formation of by-products due to accelerated aging was also evaluated by interfacial tension test that itself is indicative for the presence of polar oxidation by-products in insulating oil matrix. Fig 5.3 summarizes the formation of oxidation by-products in the presence of seven antioxidants added to oil samples individually. Based on the fact mentioned above that the lower the IFT the higher the content of polar by-products in the oil, Fig. 5.3 shows that the trend in the strength of antioxidant additives in retarding the oil oxidation would be almost similar to that deduced from the neutralization numbers in Fig. 5.2.

Again, according to interfacial tension test, oxidation by-products generated from the oil sample containing DBDS-Cu were higher than those obtained from the oil sample with DBDS only. This would add another evidence that the presence of copper strip catalyzes the effect of corrosiveness of DBDS in mineral insulating oil.

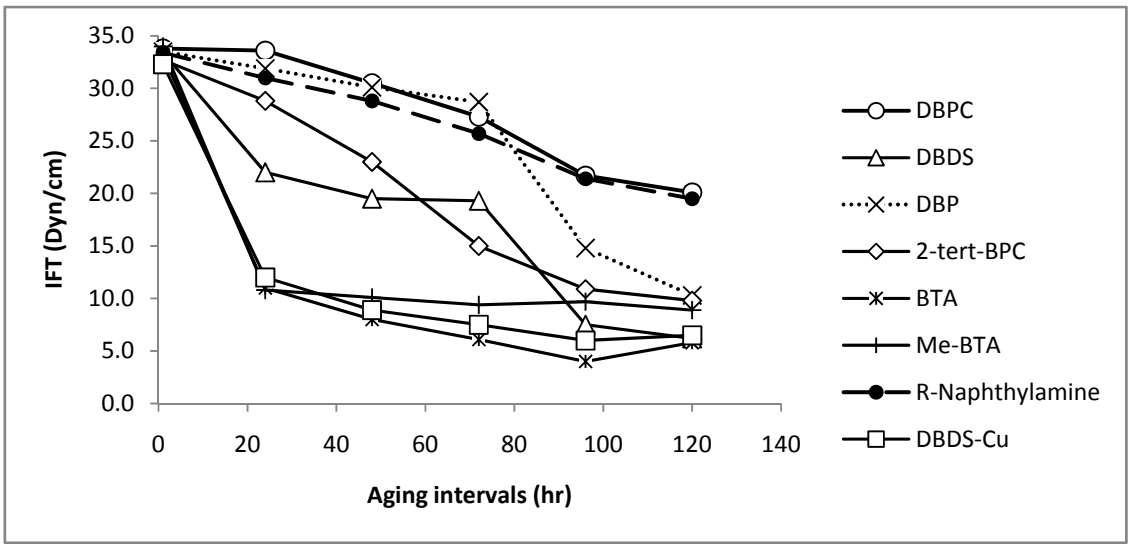


Fig 5.3. Interfacial tension after accelerated aging for several oil samples containing different antioxidants. DBDS-Cu refers to the case where a copper strip was added into the oil sample solution with DBDS.

5.3.2 Assessment of the stability of antioxidant additives

Liquid – liquid extraction followed by either GC-ECD-FID or HPLC determination was used to quantitatively detect the depletion of each antioxidant during the accelerated aging intervals. The method was sensitive enough to detect depletion of fractions of mgL^{-1}. DBDS, DBPC, DBP, 2-tBPC and alkylation-α-naphthylamine were determined by GC/ECD-FID following the liquid-liquid extraction pretreatment step. However, BTA and methyl BTA were determined by HPLC following the liquid-liquid extraction pretreatment step.

Figs. 5.4 to 5.9 demonstrate the quantitative depletion of each antioxidant added to the mineral insulating oil samples during an artificial aging process. The depletion of both BTA and methylated-BTA were found to be the most sever among all the investigated antioxidants. The signal obtained after a period of 24 h for both species was not detected indicating a poor and short lifetime antioxidants. Consequently, the depletion of these two species was not subjected to further studies. Table 5.1 and Fig. 5.10 represent the depletion rate constants for the various antioxidant additives studied. Excluding DBDS, DBPC and DBP showed relatively the lowest depletion rate constant that means the highest stability, however, BTA and methylated BTA were depleted fully after 24h as mentioned above indicating very poor stability as antioxidant additives. Generally, the trend of the depletion rate constant of antioxidant additives studied is in good agreement with that obtained for the strength of antioxidants as oxidation inhibitors in mineral oil concluded from the neutralization number and interfacial tension mentioned above [5].

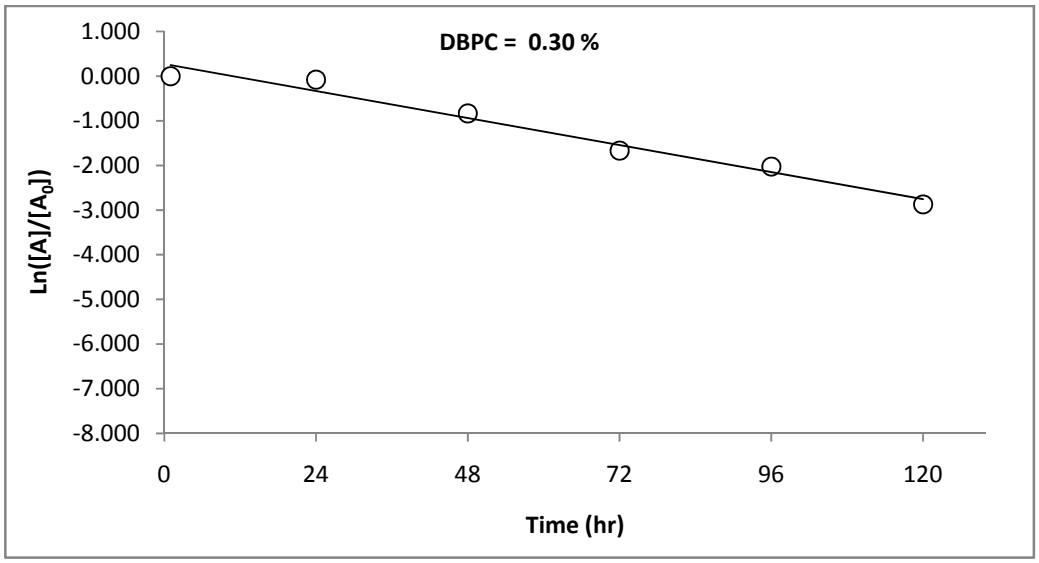


Fig. 5.4. The depletion of 0.3% w/v DBPC in mineral oil determined by the GC/FID following the liquid-liquid extraction pretreatment step.

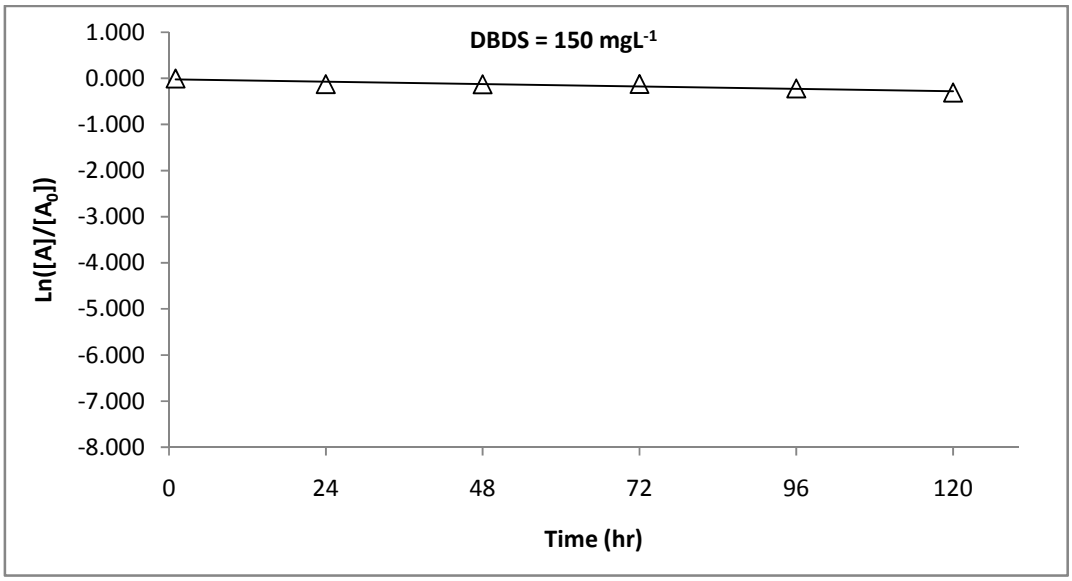


Fig 5.5. The depletion of 150 mgL^{-1} DBDS in mineral oil determined by the GC/ECD following the liquid-liquid extraction pretreatment step.

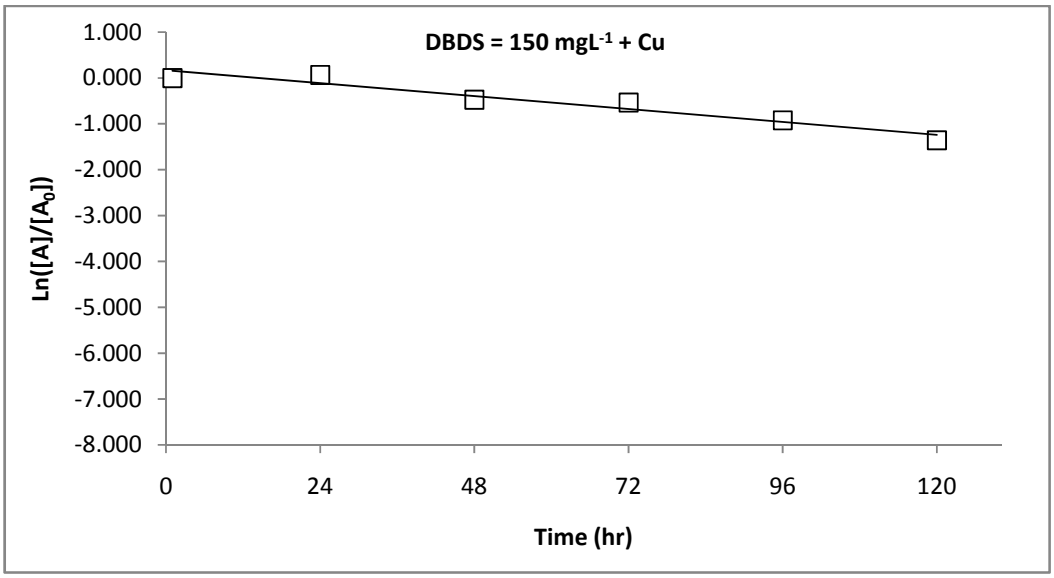


Fig 5.6. The depletion of 150 mgL^{-1} DBDS in mineral oil determined and in the presence of copper strip by the GC/ECD following the liquid-liquid extraction pretreatment step.

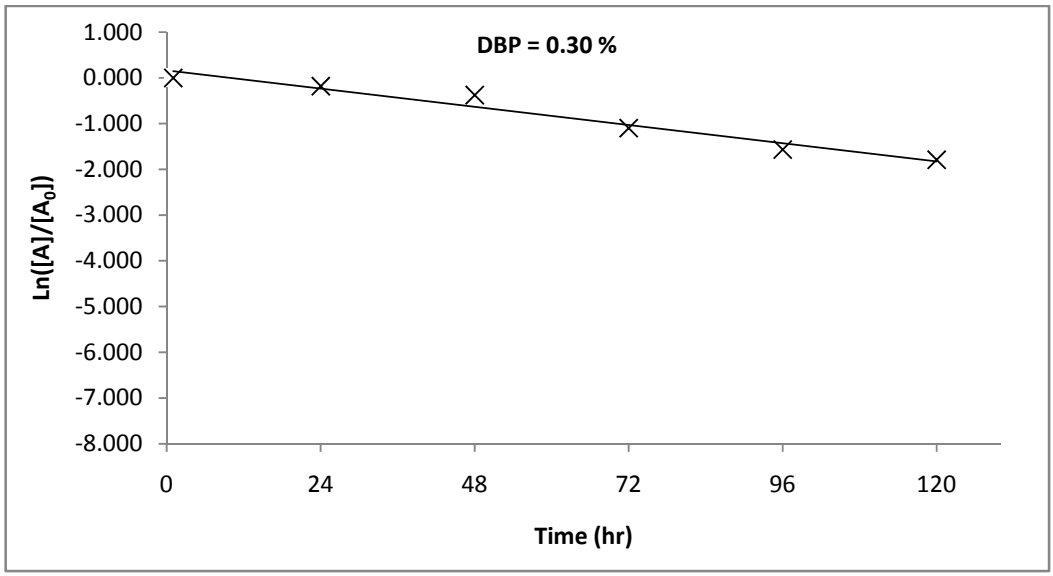


Fig 5.7. The depletion of 0.3% w/v DBP in mineral oil determined by the GC/FID following the liquid-liquid extraction pretreatment step.

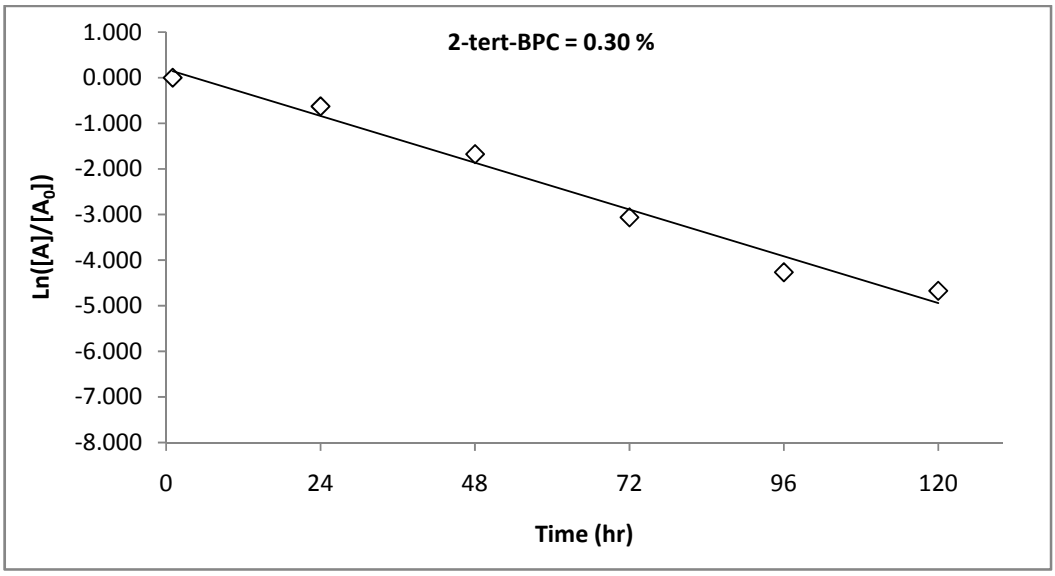


Fig 5.8. The depletion of 0.3% w/v 2t-BPC in mineral oil determined by the GC/FID following the liquid-liquid extraction pretreatment step.

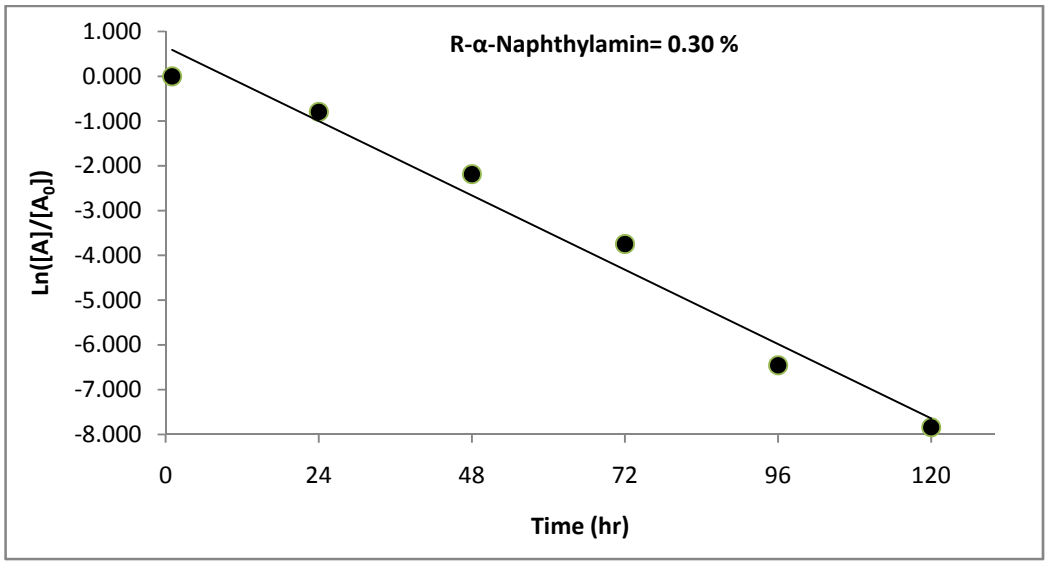


Fig 5.9. The depletion of 0.3% w/v R-α-Naphthylamin in mineral oil determined by the GC/FID following the liquid-liquid extraction pretreatment step.

Table 5.1 Depletion rate constant for various antioxidant additives

Antioxidant additive	Depletion rate constant, k (h^{-1})
DBPC	25×10^{-3}
DBDS	2.0×10^{-3}
DBDS + Cu	12×10^{-3}
DBP	17×10^{-3}
2t-BPC	43×10^{-3}
R-α-Naphthylamin	69×10^{-3}

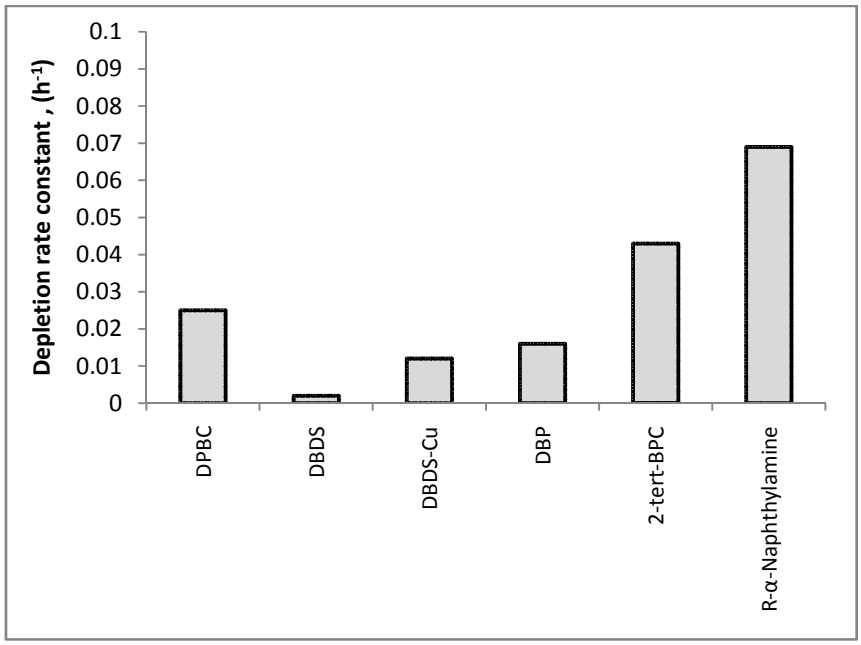


Fig 5.10. Representation of the depletion rate constants for the antioxidants added to insulating oil samples after the artificial aging according ASTM D 2440.

It is interesting to note that DBDS showed the lowest depletion rate constant over the period of accelerated oxidation. Thus, DBDS would have the highest depletion stability among all antioxidant additives studied. However, when a copper strip was added to the oil sample solution during the incubation period, the depletion rate constant has increased (Table 5.1 and Fig. 5.10) significantly. This increase would be due to the corrosion activity with the copper strip. Thus, DBDS may be considered as a very stable antioxidant agent in the mineral oil only in absence of copper.

5.4 Conclusion

The generation of acids and other by-products in the oil matrix in presence of DBPC was found to be small compared to other antioxidants. The neutralization number and the interfacial tension changes do not correlate with the depletion trend for DBPC which it shows a critical depletion trend compared to other antioxidants. This may be attributed to the short lifetime of such additive.

It is known that DBDS depletes when it reacts with copper conductors inside the transformer unit. The present study confirmed quantitatively that DBDS remains in mineral insulating oil for long time before being subjected to chemical depletion when it acts as either as antioxidant or as corrosive sulfur. Depletion rate of DBDS when it acts as an antioxidant in presence of copper was found to be less than that of DBPC or DBP whereas the depletion of DBDS in absence of copper was negligible. This may introduce another type of challenge when detecting DBDS in the oil matrix. DBDS is a stable antioxidant and may stay as part of oil matrix for long time especially in the absence of high operational

temperatures. Furthermore, high acid content released in the oil matrix when DBDS reacted with copper which consequently highlight to the corrosion problem.

BTA and its methylated derivatives are not stable antioxidants at higher operational temperature as they are severely deplete due to the formation of oxidation by-products during aging processes. Agreed with the reported works, the steric hindered phenolic antioxidants like DBPC are more preferable because the latter undergoes lower depletion compared to other phenolic and BTA antioxidants. Still the depletion of DPBC as an antioxidant is higher than those of DBDS with and without copper.

Chapter Six

Collective behavior of DBDS, DBPC, BTA and DBP in mineral insulating oils

6.1 Introduction

Several risk assessment and mitigation techniques have been suggested whenever the oil is considered as corrosive. The most widely used technique so far is the addition of a metal passivator. Both oil change and on-site oil treatment to remove corrosive components have also been applied. It is sometimes possible to modify the operating conditions in order to lower temperature and dielectric stresses. All of these approaches are considered here [9].

One obvious mitigation technique, that may be used, consists of simply replacing the existing oil in a transformer or shunt reactor unit by new, non corrosive oil. Evidently in this approach, the corrosive compound content is reduced by diluting the existing oil according to the ratio between the volume of the new oil added and the volume of the old oil remained (i.e., the existing remaining oil at the bottom of the tank and windings of the specimen unit). The latter ratio may vary from 5 to 12% depending on the amount of paper and other absorbing materials as well as the shape of the tank. In addition, prior to changing the oil, a test of corrosive sulfur on a suitable mixture of the old and new oil should be made to ascertain whether the mitigation effort is adequate to provide non corrosive oil [12].

As reported by Ren et al that, once the insulation oil used in transformers or reactors was detected as abnormal, or there was any potential risk in it, an effective way is to change all the used oil with new (unused) ones that have passed the corrosive test. However, non-corrosive sulfur on hot metal surfaces can become corrosive after being exposed to elevated temperatures and thus produce metal sulfides which create later problems [50].

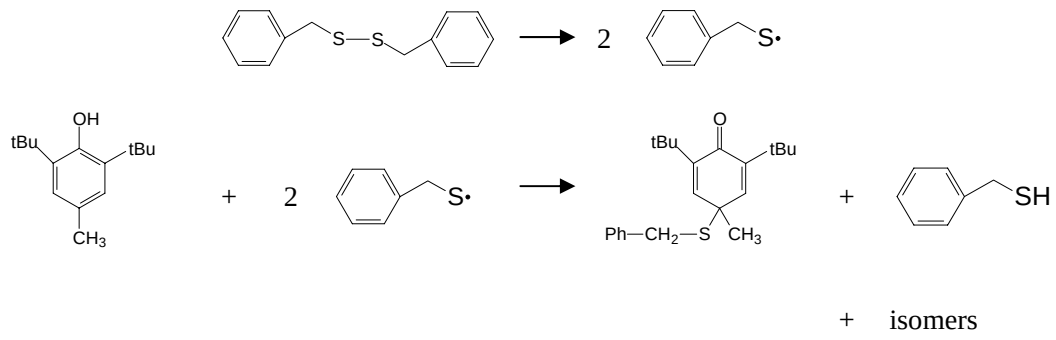
Smith et al [51] reported that replacing the oil is an expensive process and, therefore, may not be considered favorable by the plant maintenance. However, if the oil fails the standard methods IEC 62535 and ASTM D 1275, then corrosive sulfur is quite likely forming deposits which act to degrade the insulation. Depending on how long the transformer has been in service excessive damage may have already occurred. Although it is not possible to reverse the sulfur corrosion process, the remaining life of the transformer may be better preserved if the oil is replaced more frequently which is not a practical mitigation.

There is no single evidence that the deposited copper sulfide inside electrical transformer units can be removed or reversed by any suggested treatment. Even though considered as a moderately high cost procedure, oil treatment is another effective way to reduce corrosive sulfur (DBDS) in the oil matrix. There are four methods for reducing corrosive sulfur species in the oil matrix namely: oil depolarization, traditional oil reclamation, solid/liquid extraction and liquid/liquid extraction [12]. The most common treatment method which reduces corrosive sulfur species in the oil matrix is depolarization where it reduces DBDS to levels less than 5 mgL^{-1}. This treatment requires analytical method to quantify DBDS to judge the efficiency of the treatment in which it may take several cycles before concluding

the process. Oil depolarization uses a solid chemical that is required to function as a sorbent of which corrosive sulfur species are extracted from the oil. Besides, a relative high cost of such treatment, oil depolarization removes also the necessary additives in the oil matrix like passivators and other antioxidants rendering the oil as uninhibited. This adds an extra cost to the end user where a new dose of additives should be used to improve the oil quality.

Still the use of metal passivators (BTA or BTA derivatives) to quench the effect of DBDS in mineral insulating oils is the best and cost effective remedial procedure. As mentioned in Chapter four, there is a need to monitor the quantity of BTA or BTA derivatives at certain intervals. The thermal depletion of such additives brings the corrosivity again to insulating oil if DBDS is present as it was concluded in this study that DBDS is very stable antioxidant in mineral insulating oil. Being very stable species, DBDS remains in the oil even after the depletion of the metal passivator which makes the oil to be corrosive.

It was reported earlier that the synergy effect of DBPC and BTA may produce a good mitigation against corrosive sulfur. Takashi et al studied this synergy effect as a combination between DBPC, BTA and DBDS [6]. Considering DBPC as a primary antioxidant and acts as radicals trapping agent, DBDS can react with DBPC according to the following reaction:



This mechanism should reduce DBDS effect in the oil when BTA is present on copper and in the oil matrix. According to Takashi et al, DBPC attacks DBDS and removes its corrosivity and deactivates it further even if BTA depletes due to thermal factors. According to this study, several mineral oil solutions containing a known concentration of DBDS were prepared as follows: a solution of 30 mgL^{-1} BTA, a solution of 0.3% DBPC, a solution of 30 mgL^{-1} BTA + 0.3% DBPC and the last solution was prepared without the addition of any additive. All the oil samples were thermally incubated as per ASTM D 1275 criteria for several intervals. Expectedly, oil without additives showed the highest corrosivity whereas oil with BTA showed initially non-corrosive oil but at the final incubation stages the oil started to become corrosive due to BTA depletion. Solutions of oil containing both DBPC and BTA proved to be excellent in preventing corrosion. The corrosivity of oil was investigated by measuring the total sulfur signal resulting from the corrosion of the copper strips after the incubation period for each oil solution. Also the percent depletion of each additive was measured for several intervals whereas DBDS depletion in this study was not performed.

In this study, the synergy effect between three additives namely: antioxidant (DBPC), metal passivator (BTA) and corrosive sulfur (DBDS) was investigated quantitatively by targeting the depletion of each compound in the oil matrix using the liquid - liquid extraction pretreatment followed by GC/HPLC determination method presented in Chapter 2. Consequently, the collective behavior of these additives in mineral insulating oil has been studied in this work. A similar investigation was performed on another antioxidant namely, 2,6-Di-tert-butyl-phenol (DBP), to shed more light on the effect of the chemical structure of this antioxidant working as trapping agent for radicals.

6.2 Experimental and methods

Seven groups of various mineral insulating oil samples containing known concentrations of the three additives (150 mgL^{-1} DBDS, 30 mgL^{-1} BTA and 0.3% w/v DBPC) were prepared. These groups were incubated at 150^{o}C and subjected to thermal aging processes at several intervals (five days) according to IEC-62535 criteria. Each oil group consisted of six 20 ml headspace glass vials. Each vial was filled with 15 ml oil containing a known concentration (of certain additive or a mixture of additives and finally covered with aluminum cap. Group-1 represented an oil sample containing 30 mgL^{-1} BTA only. Group-2 represented an oil sample containing a combination of 30 mgL^{-1} BTA and 0.3% w/v DBPC. Group-3 represented an oil sample containing 0.3% w/v DBPC only. Group-4 represented an oil sample containing a combination of 30 mgL^{-1} BTA and 150 mgL^{-1} DBDS. Group-5 represented an oil sample containing a combination of 150 mgL^{-1} DBDS and 0.3% w/v DBPC. Group-6 was designed to represent the synergy effect between the three additives together in one oil sample that contained 150 mgL^{-1} DBDS, 30 mgL^{-1} BTA and 0.3% w/v

DBPC. Group-7 contained 150 mgL^{-1} DBDS only. Groups 8 to 14 represented the same set of groups 1 to 7 but DBPC was replaced with DBP. Copper strips covered with Kraft insulating paper were immersed in every oil sample solution. The vials were purged with argon under closed condition before incubation taking place to eliminate the atmospheric oxygen from penetration..

6.3 Results and discussion

As a means to study the collective behavior of the three additives: DBDS, DBPC/DBP and BTA, various oil samples containing different combinations of these additives at concentration levels as per the recommendation in the literature [13, 15, 16, 17, 18, 36, 50] and the real application for these compounds in mineral insulating oil matrices. These oil samples were incubated at conditions that simulate those inside a transformer unit were the accelerated thermal aging took place as per the standard method and the reported methods criteria. Table 6.1 demonstrates the details of these oil samples.

The individual behavior of DBDS was not studied here because it has been investigated in the previous chapters. Individual and the collective behavior for these additives were studied on the basis of the assessment of the depletion rate and the percent recovery of each additive at the end of the incubation interval. Copper strips covered with Kraft insulating paper were immersed in every oil sample solution where at the end of the interval, the corrosion on these strips was observed to correlate the qualitative and quantitative results.

Table 6.1 The distribution of additives, DBDS, BTA, DBPC and DBP among the various oil sample solutions in the different groups.

Group	DBDS (mgL^{-1})	BTA (mgL^{-1})	DBPC (%)	Group	DBDS (mgL^{-1})	BTA (mgL^{-1})	DBP (%)
1	-	30	-	8	-	30	-
2	-	30	0.30	9	-	30	0.30
3	-	-	0.30	10	-	-	0.30
4	150	30	-	11	150	30	-
5	150	-	0.30	12	150	-	0.30
6	150	30	0.30	13	150	30	0.30
7	150	-	-	14	150	-	-

Qualitative and quantitative investigations were performed for each individual solution by the determination of the depletion rate for every additive in each group of the oil sample solutions using the liquid – liquid extraction pretreatment followed by GC/HPLC determination. The relationship between the depletion rate and the incubation time for each additive was established.

Neutralization number was determined for each oil group at the final incubation stage of 120 h using ASTM D 974 [46]. This test measures the acids generated from the oxidation processes occurring under the effect of the thermal conditions and the interaction between the additives with each other and with the oil matrix.

Figures. 6.1 and 6.2 show the neutralization numbers found for all of the groups of oil sample solutions at the end of incubation periods (120 h). The neutralization numbers for all oil samples (group 1 to group 14) in the presence of all additives were in the range of about 0.03 to 0.06 mg KOH. These numbers are close to the acceptable neutralization number of 0.03 mg KOH which is characteristic to new oil sample according to the ASTM D 3487. Consequently, the degradation in the oil matrix as a result of thermal aging and in the presence additives according to the results of the conventional method ASTM D 974 is either absent or minimal. It is interesting to report that the conventional method ASTM D 974 was not critical in detecting the degradation behavior of oil samples in the absence and in the presence of additives.

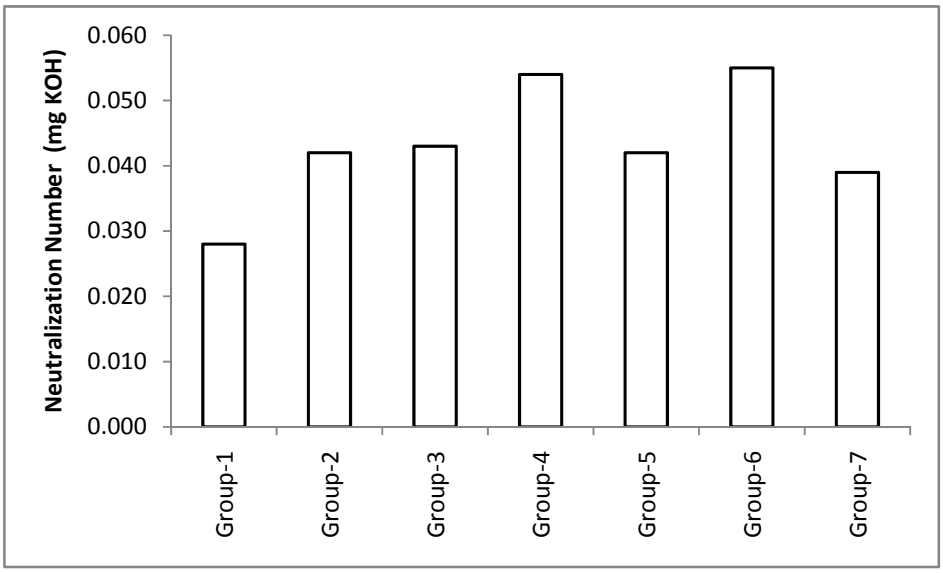


Fig 6.1. Acid content expressed as neutralization number generated from oil degradation as a result of thermal aging for mineral oil sample solution groups 1 to 7 where the primary antioxidant was DBPC. Neutralization numbers were determined for the oil sample left until the final incubation interval.

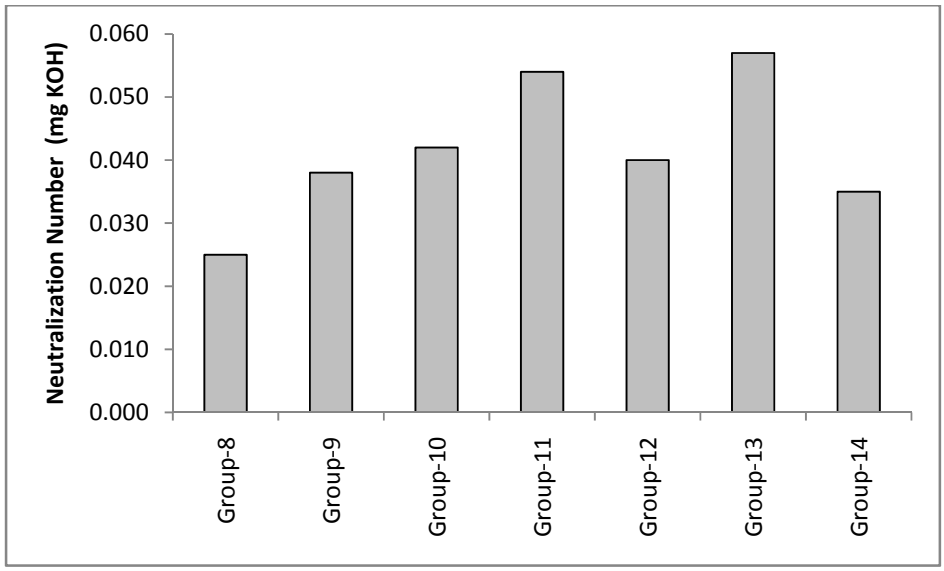
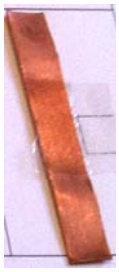


Fig 6.2. Acid content expressed as neutralization number generated from oil degradation as a result of thermal aging for mineral oil sample solution groups 8 to 14 where the primary antioxidant was DBP. Neutralization numbers were determined for the oil sample left until the final incubation interval.

In another attempt to study the thermal degradation of oil in the presence and in the absence of mineral oil additives, a qualitative investigation was carried out for copper strips discoloration for every oil sample in all oil groups. In agreement with literature conclusion [6 - 9], copper corrosion was severe for groups 7 and 14 where oil samples contained only 150 mgL^{-1} DBDS (Fig 6.3). Expectedly, groups 1, 2, 3, 8, 9 and 10 showed noncorrosive behavior because DBDS was not present in the samples of these groups (Figs 6.4, 6.5, 6.6 and 6.7). Groups 4 and 11 indicated no corrosion on copper strips at initial incubation periods till 72 h, however, discoloration on the copper strips was clearly visualized after a period of 96 h and beyond until the final interval at 120 h (Figs 6.5 and 6.7). A concentration of 30 mgL^{-1} BTA was found to prevent DBDS from acting as corrosive sulfur in groups 4 and 11.

Groups: 7 and 14	DBDS = 150 mgL^{-1}		BTA = 0 mgL^{-1}	DBPC/DBP = 0 % w/v	
Time, h	24	48	72	96	120
IEC 62535					

Fig 6.3. copper strips recovered after examination for oil groups 7 and 14 having 150 mgL^{-1} DBDS using IEC-62535 standard method.

Group: 1	DBDS = 0 mgL^{-1}	BTA = 30 mgL^{-1}	DBPC = 0 % w/v		
Time, h	24	48	72	96	120
IEC 62535					

Group: 2	DBDS = 0 mgL^{-1}	BTA = 30 mgL^{-1}	DBPC = 0.3 % w/v		
Time, h	24	48	72	96	120
IEC 62535					

Fig 6.4. copper strips recovered after examination for oil groups 1 and 2 using IEC-62535 standard method

Group: 3	DBDS = 0 mgL^{-1}	BTA = 0 mgL^{-1}	DBPC = 0.3 % w/v		
Time, h	24	48	72	96	120
IEC 62535					

Group: 4	DBDS = 150 mgL^{-1}	BTA = 30 mgL^{-1}	DBPC = 0 % w/v		
Time, h	24	48	72	96	120
IEC 62535					

Fig 6.5. copper strips recovered after IEC-62535 examination for oil groups 3 and 4 using IEC-62535 standard method.

Group: 8	DBDS = 0 mgL^{-1}	BTA = 30 mgL^{-1}	DBP = 0 % w/v		
Time, h	24	48	72	96	120
IEC 62535					

Group: 9	DBDS = 0 mgL^{-1}	BTA = 30 mgL^{-1}	DBP = 0.3 % w/v		
Time, h	24	48	72	96	120
IEC 62535					

Fig 6.6. copper strips recovered after IEC-62535 examination for oil groups 8 and 9 using IEC-62535 standard method.

Group: 10	DBDS = 0 mgL^{-1}	BTA = 0 mgL^{-1}	DBP = 0.3 % w/v		
Time, h	24	48	72	96	120
IEC 62535					

Group: 11	DBDS = 150 mgL^{-1}	BTA = 30 mgL^{-1}	DBP = 0 % w/v		
Time, h	24	48	72	96	120
IEC 62535					

Fig 6.7. copper strips recovered after IEC-62535 examination for oil groups 10 and 11 using IEC-62535 standard method.

Unlike the conclusion reported previously in the literature [6], in this study it was found that DBPC does not prevent the corrosion behavior of DBDS in groups 5 and 12 where copper sulfide formation was visible after an incubation period of 24 h for both groups (Figs 6.8 and 6.9). Also, as per Figs 6.8 and 6.9, Groups 6 and 13 exhibited the best corrosion prevention even after the end of the incubation interval (120 h). Unlike the case of groups 4 and 11 where a minor discoloration was detected visually at 96 and 120 h in both of them due to BTA thermal depletion, 30 mgL^{-1} BTA in groups 6 and 13 was able to quench copper sulfide formation in the presence of 150 mgL^{-1} DBDS at longer incubation periods. This finding is in good agreement with the literature [6] where BTA decomposed at the end of the incubation periods and as a result DBDS attacks copper strip and copper sulfide is formed (groups 4 and 11) whereas the presence of 0.30% w/v DBPC helps BTA to retain longer in the oil matrix before decomposing (groups 6 and 13).

Finally, the quantitative investigation of the synergy effect for the primary antioxidants, DBPC and DBP, with BTA to prevent the corrosion process was clearly verified by using liquid – liquid extraction pretreatment followed by GC/HPLC determination method. The depletion in each additive was investigated along with the incubation interval. In addition, the depletion rate constants were calculated for every additive in each oil group. Figs. 6.10 and 6.11 indicate that the BTA depletion was identical in groups 1, 2, 4, 6, 8, 10 11, and 13.

Group: 5	DBDS = 150 mgL^{-1}		BTA = 0 mgL^{-1}	DBPC = 0.3 % w/v	
Time, h	24	48	72	96	120
IEC 62535					

Group: 6	DBDS = 150 mgL^{-1}		BTA = 30 mgL^{-1}	DBPC = 0.3 % w/v	
Time, h	24	48	72	96	120
IEC 62535					

Fig 6.8. copper strips recovered after IEC-62535 examination for oil groups 5 and 6 using IEC-62535 standard method.

Group: 12	DBDS = 150 mgL^{-1}	BTA = 0 mgL^{-1}	DBP = 0.3 % w/v		
Time, h	24	48	72	96	120
IEC 62535					

Group: 13	DBDS = 150 mgL^{-1}	BTA = 30 mgL^{-1}	DBP = 0.3 % w/v		
Time, h	24	48	72	96	120
IEC 62535					

Fig 6.9. copper strips recovered after IEC-62535 examination for oil groups 12 and 13 using IEC-62535 standard method.

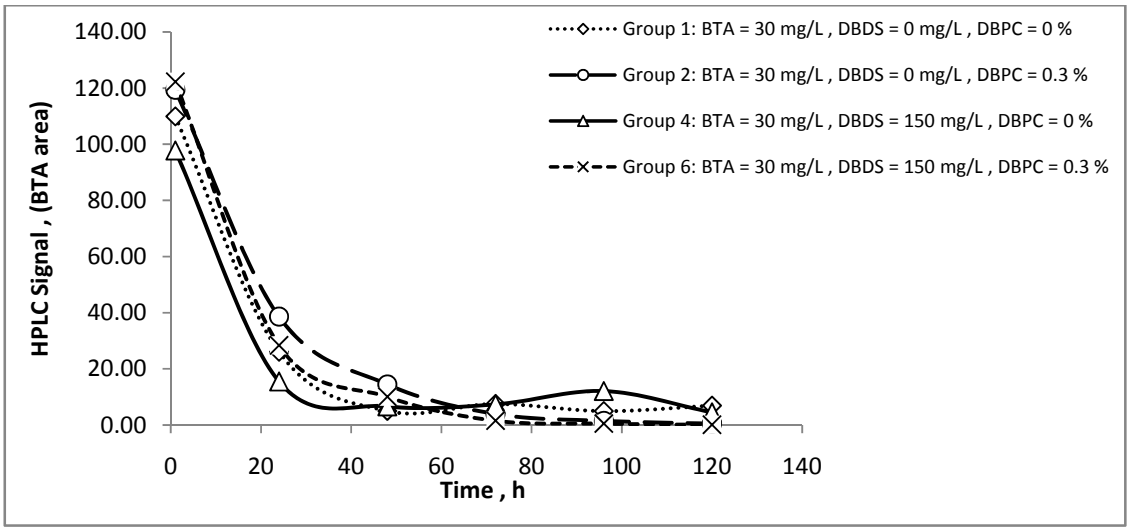


Fig 6.10. The depletion of BTA expressed as a decrease in the HPLC signal for oil sample solutions of groups 1, 2, 4 and 6

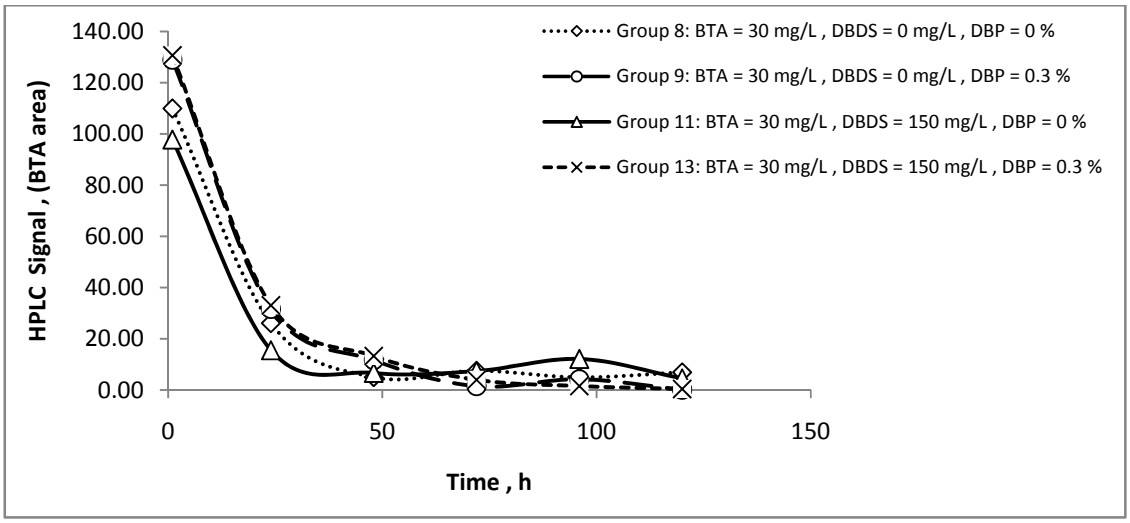


Fig 6.11. The depletion of BTA expressed as a decrease in the HPLC signal for oil sample solutions of groups 8, 9, 11 and 13

It was noted that the depletion of BTA in groups 2, 6, 9 and 13 contradicts the observation noted by other researchers [C-1] [N2] [O] [H]. These researchers have suggested that the consumption of BTA in insulating oil under thermal conditions of incubation is suppressed in the presence of DBPC. Thus, the presence of DBPC or DBP does not prevent the degradation of BTA at the final incubation stage as expected.

Moreover, unlike previous reports, neither DBPC nor DBP showed a critical depletion under the thermal incubation (Figs. 6.12 and 6.13). According to the mechanism of the reaction of DBPC with DBDS [H] given above, In groups 5, 6, 12 and 13, it was expected from this experimental trial that either DBPC or DBP would be consumed due to a reaction with DBDS where corrosion cycle could be prevented. However Figs 6.12 and 6.13 show no DBPC or DBP depletion over the whole incubation periods. Consequently, the effect of these antioxidants is not significant in case of corrosive sulfur.

Figs. 6.14 and 6.15 illustrate the depletion of DBDS due to the corrosion process. However, as was mentioned earlier, the depletion of DBDS as an antioxidant is found to be negligible whereas its depletion due to corrosion is clearly severe in the presence of copper. Groups 5 and 7 (Fig. 6.14) showed almost no depletion in DBDS. On the other hand, the depletion profiles of DBDS in groups 4 and 6 (Fig. 6.14) were found to be identical, which indicates that the performance of DBPC was not effective as a corrosion inhibitor. The same argument is valid for groups 11, 12, 13, and 14. The depletion in DBDS for all related groups shows that the synergy effect has no significant effect in preventing copper sulfide formation.

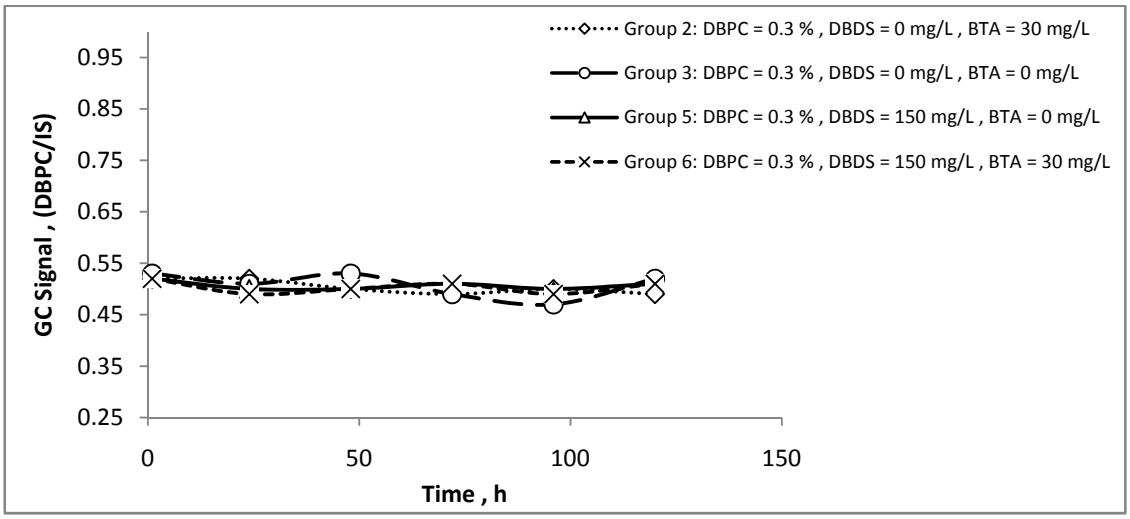


Fig 6.12. The depletion of DBPC expressed as a decrease in the GC-FID signal for oil sample solutions of groups 2, 3, 5 and 6.

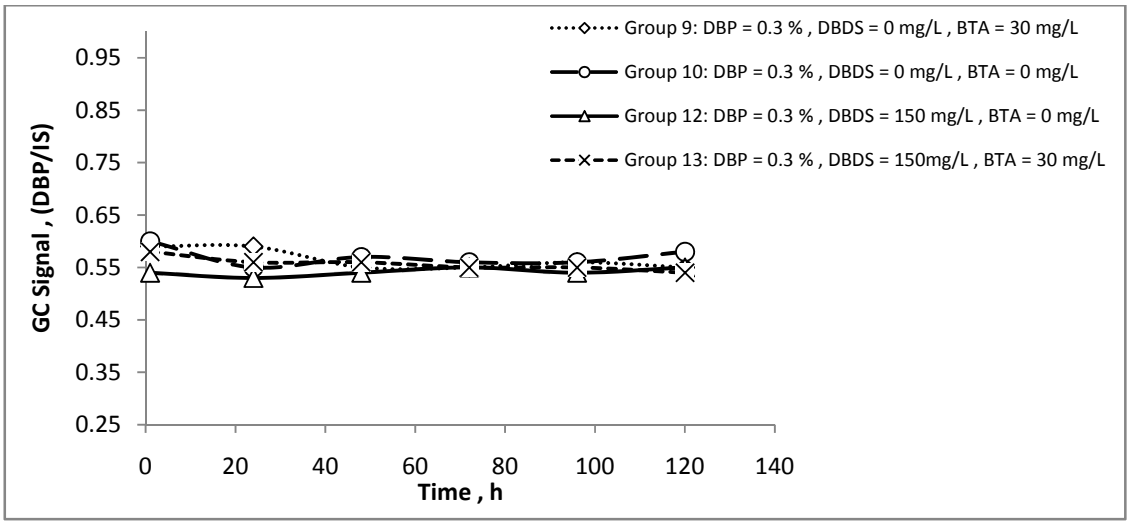


Fig 6.13. The depletion of DBP expressed as a decrease in the GC-FID signal for oil sample solutions of groups 9, 10, 12 and 13.

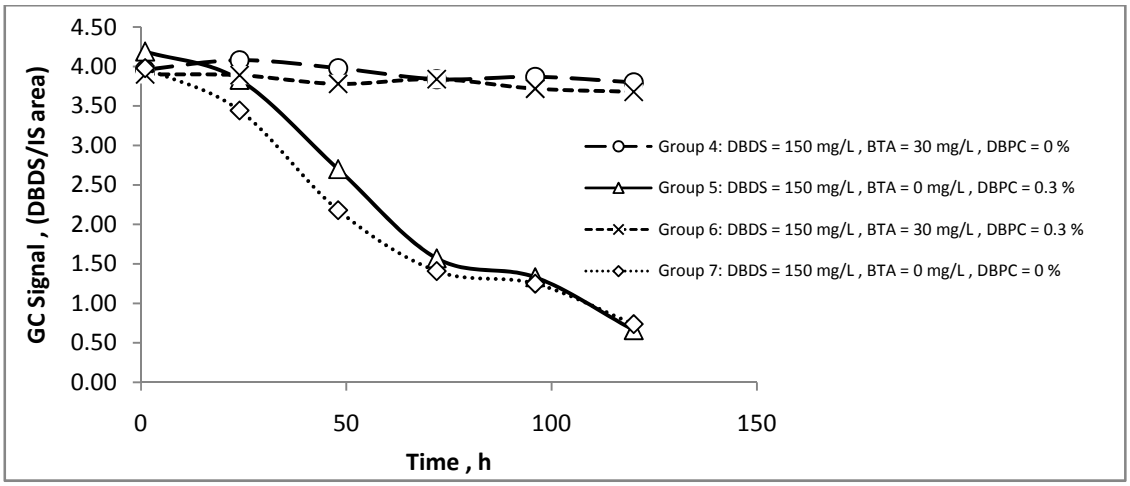


Fig 6.14. The depletion of DBDS expressed as a decrease in the GC-ECD signal for oil sample solutions of groups 4, 5, 6 and 7.

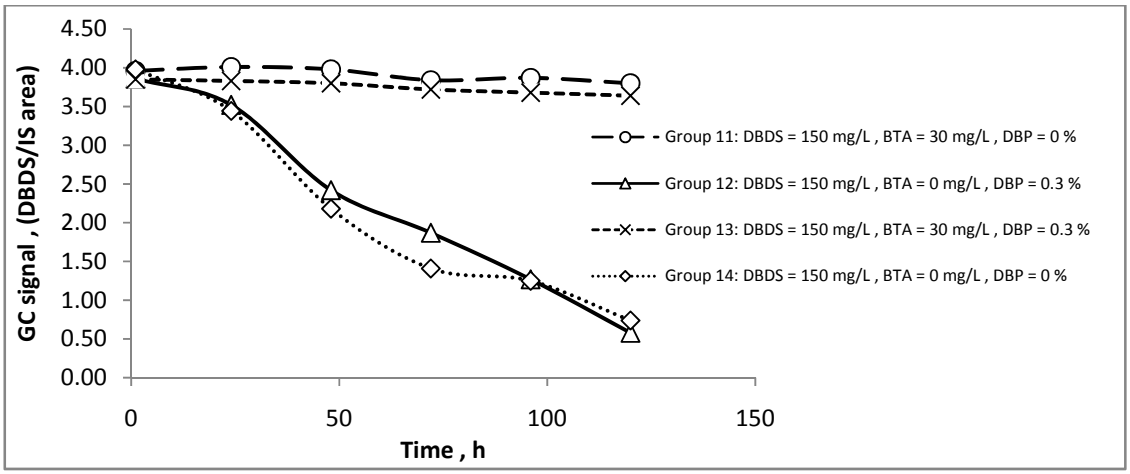


Fig 6.15. The depletion of DBDS expressed as a decrease in the GC-ECD signal for oil sample solutions of groups 11, 12, 13 and 14.

The depletion rate constants for each additive in the incubated oil samples were determined from the above experiments and listed in Tables 6.2 and 6.3. The calculated depletion rate constants for each additive confirm the synergy effect is insignificant when both BTA and DBPC are present in the oil matrix simultaneously and this is in agreement to the conclusion mentioned above. The depletion rate of BTA is the highest for oil samples of groups 2, 6, 9 and 13 where DBPC and DBP were present respectively. Using the same argument for BTA, the depletion rate constant for DBDS recorded the highest values for oil samples of groups 5 and 12 where DBPC or DBP were present with DBDS in these oil samples. The calculated depletion rate constants for DBDS with both primary antioxidants (DBPC and DBP) in the oil samples of groups 5 and 12 were comparable with the depletion rate constants of DBDS alone in the oil samples of groups 7 and 14. These results indicate that the effect of DBPC or DBP on DBDS depletion as per the above mentioned mechanism is not significant.

6.4 Conclusion

From this work one can conclude that the synergy effect for antioxidants like DBPC and DBP on both BTA and DBDS is insignificant. DBPC as well as DBP have demonstrated a steady depletion condition with almost stable signals along the incubation periods. On contrary, DBDS and BTA suffered from severe depletion even in presence of any of the antioxidants. It was found that, only the presence of BTA in mineral insulating oils suppresses the depletion of DBDS as corrosive species and prohibited copper sulfide formation. In spite of being a good suppressor for copper corrosion, BTA concentration should be monitored regularly to avoid the thermal depletion otherwise the corrosive

behavior of DBDS becomes effective. The rate constants for DBDS indicate that this compound behaves as corrosive sulfur only in the absence of BTA.

Table 6.2- Depletion rate constants of three additives incubated according to the standard method IEC 62535 and determined by the liquid-liquid extraction pretreatment followed by GC/HPLC determination methods

Group	k_{BTA} ($\times 10^3$ h^{-1})	k_{DBDS} ($\times 10^3$ h^{-1})	k_{DBPC} ($\times 10^3$ h^{-1})
1	21.9	-	-
2	46.0	-	0.5
3	-	-	0.5
4	19.1	0.5	-
5	-	15.5	0.1
6	60.6	0.5	0.1
7	-	14.3	-

Table 6.3 Depletion rate constants of three additives incubated according to the standard method IEC 62535 and determined by the liquid-liquid extraction pretreatment followed by GC/HPLC determination methods

Group	k_{BTA} ($\times 10^3$ h^{-1})	k_{DBDS} ($\times 10^3$ h^{-1})	k_{DBP} ($\times 10^3$ h^{-1})
8	21.9	-	-
9	54.0	-	0.6
10	-	-	0.2
11	19.1	0.5	-
12	-	15.3	0.1
13	47.1	0.5	0.5
14	-	14.3	-

References

1. H. G. Erdman, "Electrical Insulating Oils", American Society for Testing Material, Philadelphia (1987), pp 47.

2. M. Horning, J. Kelly, S. Myers, R. Stebbins, "Transformer Maintenance Guide", 3rd ed, (2004), pp. 50 – 177.

3. S. Myers, J. Kelly, R. Parrish, "A Guide to Transformer Maintenance", 1st ed.,(1981). pp. 156 – 157.

4. R. Criso´stomo Rabelo Neto, Daniel O. Lima, Thauzer D. S. Pinheiro, Roˆmulo F. Almeida, Tereza N. Castro Dantas, Michelle S. G. Dantas, M. Adelina S. Arau´ jo, Ce´ lio L. Cavalcante, Jr., and Diana C. S. Azevedo, "Thermo-Oxidative Stability of Mineral Naphthenic Insulating Oils: Combined Effect of Antioxidants and Metal Passivator", *Appl. Chem*., (2004), pp. 7428 – 7434.

5. J. Hao, R. Liao, S. Liang, L. Yang, M. Zhu, Proceedings of the 9th International Conference on Properties and Applications of Dielectric Materials, July (2009), Harbin, China, pp 53 – 56.

6. T. Ito, Y. Morishima, "Corrosion Control by Antioxidant DBPC in Insulating Oil", *IEEJ Trans*., Vol. 4, (2009), pp. 422 – 424.

7. ASTM D 3487, Standard Specification for Mineral Insulating Oil, *ASTM International*, Vol. 10.03, (2006).

8. P. Griffin, L. Lewand, Transmission & Distribution World, (2006), 34.

9. CIGRE WG A2-32, "Copper sulfide in transformer insulation", Final report – Boucher 378 , (2009).

10. Maina R., Scatiggio F., Kapila S., Tumiatti V., Tumiatti M. and Pompili M. "Dibenzyl disulfide (DBDS) as corrosive sulfur contaminant in used and unused mineral insulating oils" published on CIGRE SC2 web site, (2006).

11. V. Tumiatti, M. Tumiatti, R. Maina, C. Roggero, " Integrated Methods for the Determinations of Corrosivity, Aging, Fingerprinting as well as the Diagnosis, Decontamination, Depolarization and Detoxification of Mineral Insulating Oils and Transformers" *Sea Marconi Technologies Sas*, Italy, (2009).

12. R. Maina, V. Tumiatti, M. Pompili, R. Bartnikas, "Corrosive Sulfur Effects in Transformer Oils and Remedial Procedures", *IEEE Trans*, Vol. 16, No. 6, (2009), pp. 1655 – 1663.

13. M. Augsta, G. Martins, A. Gomes, "Experimental Study of the Role Played by Dibenzyl Disulfide on Insulating Oil Corrosivity – Effect of Passivator Irgamet 39", *IEEE Electrical Insulating Mag.*, Vol. 26, No.4, (2010), pp. 27 – 32.

14. H. Kawarai, Y. Fujita, J. Tanimura, S. Toyama, N. Yamada, E. Nagao, "Role of Dissolved Copper and Oxygen on Copper Sulfide Generation in Insulating Oil", *IEEE*, Vol. 16, No. 5, (2009), pp. 1430 – 1433.

15. T. Amimoto, N. Hosokawa, E. Nagao, J. Tanimura, S. Toyama, "Concentration dependence of corrosive sulfur on copper-sulfide deposition on insulating paper used for power transformer insulation", *IEEE Trans*, Vol. 16, No. 5, (2009), pp. 1489 – 1495.

16. T. Amimoto, E. Nagao, J. Tanimura, S. Toyama, N. Yamada, "Duration and Mechanism for Suppressive Effect of Triazole-base Passivators on Copper-sulfide Deposition on Insulating Paper", *IEEE Trans*, Vol. 16, No. 1, (2008), pp. 257 – 264.

17. T. Amimoto, E. Nagao, J. Tanimura, S. Toyama, Y. Fujita, H. Kawarai, N. Yamada, "Identification of affecting factors of copper sulfide deposition on insulating paper in oil", *IEEE Trans*, Vol. 16, No. 1, (2009), pp 265 – 272.

18. F. Scatiggio, M. Pompili, R. Bartnikas, “Oils with presence of corrosive sulfur: Mitigation and collateral effects”, 2009 *IEEE Electrical Insulation Conference, Montreal, Canada*, 31st May – 3rd June (2009).

19. Scott. G, Atmospheric Oxidation and Antioxidants, *Elsevier*, Amsterdam – London - New York, (1965).

20. S. Toyama, J. Tanimura, N. Yamada, E. Nagao,” Highly Sensitive Detection Method of Dibenzyl Disulfide and the Elucidation of the Mechanism of Copper Sulfide Generation in Insulating Oil”, *IEEE Trans*., 16, (2009), 509 – 515.

21. P. Wiklund, M. Levin, B. Pahlavanpour, “Copper Dissolution and Metal Passivators in Insulating Oil”, *IEEE*, Vol. 23, No. 4, (2007), pp. 1 – 14.

22. J. Shin, J. Hong, “ Effect of the Addition of Benzotriazole on the Streaming Electrification Properties in Transformer Oil”, *Trans. Elect. Electron. Mater*, Vol. 11, No. 6, (2010), pp. 288 – 291.

23. P. Wiklund, “ Chemical Stability of Benzotriazole Copper Surface Passivators in Insulating Oils”, *Ind. Eng. Chem. Res*, Vol. 46, No. 10, (2007), pp. 3312 – 3316.

24. B. Pahlavanpour, K. Sundkvist, Nynas Naphthenics Ltd, Application Notes, UK, Dec (2007).

25. IEC 62535, “Insulating liquids - Test method for detection of potentially corrosive sulfur in used and unused insulating oil”, *IEC*, (2008).

26. ASTM D1275-06, “Standard Test Method for Corrosive Sulfur in Electrical Insulating Oils”, *ASTM International*, (2006).

27. ASTM D 130-04, “Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test”, *ASTM International*, (2006).

28. D. H. Grant, “Qualification of Reactive Sulfur in Transformer Oil”, IEEE Electrical Institution Conference – Canada, June 2009, pp. 489 – 490.

29. IEC 62697-1, “Insulating liquids - Quantitative determination of corrosive sulfur compounds in used and unused insulating liquids - Part 1: Test method for quantitative determination of dibenzyl disulfide (DBDS)”, *IEC*, ed. 01, (2010).

30. T. Ito, Y. Morishima,” Qualitative Evaluation of Corrosive Sulfur in Electrical Insulating Oil”, *IEEJ Trans*., Vol. 3, (2008), pp. 313 – 316.

31. ASTM D 4768-03, “Standard Test Method for Analysis of 2,6-Ditertiary-Butyl Para Cresol and 2,6-Ditertiary-Butyl Phenol in Insulating Liquids by Gas Chromatography”, *ASTM International*, (2008).

32. A. Lamarre, C. Gendron,” Analysis of 2,6-di-tert- butyl-p-cresol in Insulating Oils by High-performance Liquid Chromatography”, *IEEE Trans.*, Vol. 2, No. 3, (1995).

33. ASTM D 2668-07, “Standard Test Method for 2,6-*di*-*tert*-Butyl-*p*-Cresol and 2,6-*di*-*tert* Butyl Phenol in Electrical Insulating Oil by Infrared Absorption”, *ASTM International*, (2008).

34. L. Foley, F. M. Kimmerle, “Pulse Voltammetric Determination of Butylated Hydroxy Toluene in Transformer oils”, *Anal. Chem*. Vol. 51, No. 7, (1979), pp. 818-822.

35. M.M. Delgado-Zamarreño, I. González-Maza, A. Sánchez-Pérez and R. Carabias Martínez, “Analysis of synthetic phenolic antioxidants in edible oils by micellar electrokinetic capillary chromatography”, F*ood Chem*., Vol. 100, (2007), pp. 1722-1727.

36. M. Augusta, G. Martins, A. Gomes, B. Pahlavanpour, "Experimental Study of a Passivated Oil Corrosiveness, After Depletion of the Passivator", *IEEE*, Vol. 25, No. 6, (2009).

37. ASTM WK 24216, "Test Method for Benzotriazole (BTA) and Irgamet 39 in Electrical Insulating oil by High Performance Liquid Chromatography (HPLC)", *ASTM International*, (2009).

38. IEC 60666, "Detection and determination of specified additives in mineral insulating oils", *IEC*, ed. 02, (2010).

39. IEC 60296, "Fluids for Electrotechnical Applications – Unused Mineral Insulating Oils for Transformer and Switchgear", *IEC*, ed. 03, (2003).

40. ASTM D 5837, "Furanic Compounds in Electrical Insulating Liquids by High-Performance Liquid Chromatography (HPLC)", *ASTM International*, (2006).

41. J. C. Miller, J. N. Miller, Statistics and Chemometrics for Analytical Chemistry, 5th ed., Pearson, Harlow, (2005), pp. 121, 39.

42. P. R. Krishnamoorthy, S Vijayakumar, K. R. Krishnaswamy, P. Thomas, "Effect of Benzatriazol and 2,6 ditertiary Butyl Paracresol on the Accelerated Oxidation of New and Reclaimed Transformer Oils – A Comparative Study", Proceedings of 3rd International Conference on Properties and Applications of Dielectric Materials, Tokyo-Japan, (1991), pp. 732 – 735.

43. J. P. Percherancier, P. J. Vurchex " Fourier Transform Infrared (FT-IR) Spectroscopy to Detect Additives and Contaminants in Insulating Oils ", *IEEE Electrical Insulating Mag.*, Vol. 14, No. 3, (1998), pp. 23 – 29.

44. ASTM D 2440, "Oxidation Stability of Mineral Insulating Oil", *ASTM International*, (2004).

45. IEC 61125, "Unused Hydrocarbon Based Insulating Liquids – Test Method for Evaluating the Oxidation Stability", *IEC*, ed. 01, (1992).

46. ASTM D 974, "Acid and Base Number by Color Indicator Titration", *ASTM International*, (2007).

47. ASTM D 971, "Interfacial Tension of Oil Against Water by Ring Method", *ASTM International*, (2004).

48. ASTM D 2272, "Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel", *ASTM International*, (2004).

49. F. Scatiggio, V. Tumiatti, R. Maina, M. Tumiatti, M. Pompili. R. Bartnikas " Corrosive Sulfur Induced Failures in Oil-Filled Electrical Power Transformers and Shunt Reactors", *IEEE Trans*., 24, (2009), 1240 – 1248.

50. S. Ren, Y. Xu, X. Cao, L. Zhong, Q. Yu, R. Jeanjean. "A Research Summary of Corrosive Sulfur in Mineral Oils", Proceedings of 9th International Conference on Properties and Applications of Dielectric Materials, Harbin-China, (2009), pp. 353 – 356.

51. J. R. Smith, PE, P.K. Sen "Corrosive Sulfur in Transformer Oil", *IEEE*, (2010).

52. S. Rachmilovich, A. Masarwa, N. Meyerstein, D. Meyerstein, *Inorganic Biochemistry*, 105, (2011), 669 – 674.

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